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ARSENIC

BY

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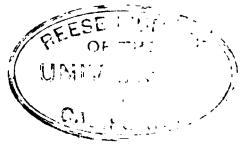

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1901

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At the Ballantyne Press

PREFACE

In the preface to a book like that which is now placed before the English readers, a little personal detail is not altogether uncalled for. The author is now an old English chemist who has been recognised as a chemist —at any rate in France and Germany—for forty-three years. Reference to such authorities as Poggendorff's Biographical Dictionary, published about the year 1862, will disclose the name of the author, and the English reader (if he should happen to be able to read German) may learn how it came to pass that the author of this book came to be looked upon as a chemist in the year 1858.

The author was brought up to the medical profession, served an old-fashioned apprenticeship in Manchester, and duly presented himself for examination, and passed the College of Surgeons in London in the year 1856. At that date the author occupied the humble, but very responsible position of private assistant to Frankland, the well-known eminent chemist. The popular excitement over the then recent Palmer case was at its height, and accusations of having

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responsible for all the cases of peripheral neuritis at present laid to its charge."*

The author of this book believes that the Manchester epidemic is chronic arsenical poisoning, and that arsenic in sufficient quantity may have existed in the beer, but that it existed in *organo-metallic combination* in a state in which it would escape recognition by the ordinary tests as applied by the analysts.

Apart, however, from the circumstances of this special outbreak many questions arise, which invest the chemistry of arsenic with interest.

Arsenic in its commonest form—common arsenic, as it is called—has, for generations, stood out as the typical poison. And terrible is Orfila's description of a typical case of acute arsenical poisoning. I quote Orfila's description from a well-known text-book published early in the last century. The poison in acute cases begins to take effect in about a quarter of an hour, and then—"An austere taste in the mouth; frequent ptyalism; continual spitting; constriction of the pharynx and œsophagus; teeth set on edge; hiccups; nausea; vomiting of brown or bloody matter; anxiety; frequent fainting fits; burning heat at the precordia; inflammation of the lips, tongue, palate, throat, stomach; acute pain of stomach, rendering the mildest drinks intolerable; black stools of an

* *British Medical Journal*, 12th January 1901, p. 85. See Paper on the "Toleration of Arsenic," by Robert W. Mackenna, M.A., M.B., Ch.B. Edin., Clinical Assistant to the Liverpool Skin Hospital.

indescribable fœtor; pulse frequent, oppressed and irregular, sometimes slow and unequal; palpitation of the heart; syncope; unextinguishable thirst; burning sensation over the whole body, resembling a consuming fire; at times an icy coldness; difficult respiration; cold sweats; scanty urine, of a red or bloody appearance; altered expression of countenance; a livid circle round the eyelids; swelling and itching of the whole body, which becomes covered with livid spots, or with a miliary eruption; prostration of strength; loss of feeling, especially in the feet and hands; delirium, convulsions" . . .; "loss of the hair, separation of the epidermis; horrible convulsions and death." The French was translated by Dr. Andrew Ure, from whose book, published in 1824, the above passage is quoted.

One of the most wonderful facts in connection with the action of arsenic on the human subject is the tolerance of arsenic acquired by the Styrian peasantry. The Styrian arsenic-eater is in the habit of taking a dose of arsenic which, if administered to one of ourselves, would bring on the frightful succession of symptoms just described.

In Johnston's "Chemistry of Common Life," published rather more than forty years ago, some particulars of the Styrian arsenic-eating are brought forward. In vol. ii., second edition, page 193, the following may be read:—

"Arsenic is thus consumed chiefly for two purposes

—First, to give plumpness to the figure, cleanness and softness to the skin, and beauty and freshness to the complexion. Secondly, To improve the breathing and give longness of wind, so that steep and continuous heights may be climbed without difficulty and exhaustion of breath. Both these results are described as following almost invariably from the prolonged use of arsenic either by men or by animals."

Arsenic-eaters, as might be expected, commence the practice of arsenic-eating by taking small doses of common arsenic. Less than half-grain doses are taken to begin with, two or three times in the week. The dose is very gradually and cautiously increased until it reaches about two grains; and this practice of arsenic-eating may be continued for forty years without apparent detriment to the system.

Recent medical experience points to arsenic as one of the most potent medicinal agencies at the disposal of the physician. That it is a specific in cases of phthisis has been asserted, and may be true to some extent.

The form of arsenic recommended for employment for this purpose is Bunsen's kakodylic acid, the marvellous substance containing rather more than half its weight of metallic arsenic and yet, notwithstanding that it is very soluble in water, absolutely non-poisonous. More than sixty years have elapsed since Bunsen's discovery of this wonderful compound of arsenic, and it is only within the last few years that

the attention of the medical profession has been called to the possibilities of a remedy of this description.

In the proper place, later on in this book, a very detailed description of this substance will be given, and its various chemical relationships set forth.

Under certain conditions, which are possible and by no means unlikely of realisation in the human body, chemical changes might be set up which would transform kakodylic acid into a deadly poison.

The reflection arises that there is pressing need for diligent study of the chemistry of arsenic, if substances like kakodylic acid are to come into use in medicine.

CHAPTER I.

CHEMISTRY OF ARSENIC.

Section 1.—*Arsenic in general, Arsenic in the free or metallic state.*

ARSENIC in the form of the sulphuret and the oxide, which is the arsenic of commerce, was known in very ancient times, and is said to have been mentioned by Avicenna in the eleventh century, and received its name in token of its poisonous nature.

When the common arsenic of commerce was first reduced so as to yield its metallic constituent is not on record; but to Brandt, in the year 1733, is due the credit of carrying out the earliest methodical investigation into the chemical character of arsenical substances, and showing that they contain a peculiar metallic substance existing in all of them in a state of chemical combination.

In the year 1755 the Swedish chemist, Scheele, discovered arsenic acid and the gas, arseniuretted hydrogen.

Proust made fairly accurate analyses of the two oxides of arsenic—analyses only differing by a few

tenths per cent. from that which is, at the present day, accepted as the correct figures — which are duly recorded in publications dating within a few years of the year 1800; showing, indeed, that certain arsenical compounds afforded some of the earliest instances of fair quantitative accuracy in chemistry.

The atomic weight of arsenic was determined by Berzelius, and also — and quite independently — by Pelouze: and the figure 75.0 is accepted by chemists. The symbol for arsenic is As = 75.

In the older books, issued at the beginning of the nineteenth century, arsenic is spoken of as one of the *semi-metals*, and that designation holds good at the present day. In the elementary state arsenic possesses one of the characteristics of metals, in a high degree, viz. metallic lustre, but the general character of its compounds is that rather of a non-metal. In its compounds it resembles phosphorus more closely perhaps than any other element. It is a triad and a pentad; and, as will be related later on, it possesses pre-eminently the power of entering into intimate organic combination with carbo-hydrogens.

Arsenical compounds, at the ordinary temperature, do not undergo reduction so as to yield elementary, or metallic arsenic; but, *at a low red heat and at higher temperatures*, arsenical compounds are very prone to undergo reduction to the metallic state.

Some arsenical compounds (arseniuretted hydrogen for instance) *simply* fall to pieces *when they are heated*

to low redness, and as the temperature is lowered, metallic arsenic is deposited in a solid state. Other arsenical compounds require the presence of some appropriate reducing agent in order that the arsenic may assume the metallic state when they are heated. Some again may need, as a preliminary, a roasting in air; but almost all arsenical compounds evolve metallic arsenic by heating to redness in a reducing atmosphere, or in an atmosphere alternately oxidising and reducing. The extreme ease with which arsenic is reduced has almost become proverbial among chemists, and forms one of the most striking analytical characters of that substance.

The production of arsenic on the large scale is thus described in a well-known modern text-book. Native arsenide of iron, or arsenical pyrites FeAsS contained in earthen retorts or tubes, is heated in a furnace; the whole of the arsenic then distils off, leaving a residue of iron or of sulphuret of iron in the retorts. The retorts are laid horizontally in the furnace, and tubes made out of thin iron plates rolled up into the form of a tube are inserted into the mouths of the retorts and an earthenware receiver is luted on. The arsenic condenses chiefly in the iron tube, and when the tube has cooled is detached by unrolling the tube. By operating in that manner the arsenic is obtained in the form of a compact mass which is nearly white.

At Altenberg in Silesia metallic arsenic is obtained by heating arsenious acid with charcoal in earthen

crucibles covered by conical iron caps or by earthen inverted crucibles; but, though the yield is larger, the quality is not so good as in the first described process, the arsenic being pulverulent and grey.

Sulphuret of arsenic may be reduced to metallic arsenic by heating it with black flux (a mixture of two parts of cream of tartar and one of nitre previously ignited) in a crucible covered with an inverted crucible luted to it with clay and sand. The arsenic forms a sublimate on the inside of the inverted crucible.

Metallic arsenic passes, without first melting, into the form of vapour at a temperature not very far removed from the boiling-point of mercury. The arsenical vapour condenses on cooling and yields a solid, the appearance of which varies according to the physical conditions to which it is subjected. During the melting the metal emits a disagreeable smell like garlic, which is said to be very characteristic. The colour of metallic arsenic has been variously described. Steel-grey says one modern author; bluish-white, the colour subject to tarnish, becoming yellowish and ultimately black on exposure to the air, says an old author.

Metallic arsenic is very brittle and may be easily powdered. It crystallises in rhombohedrons.

It is lighter than antimony, its specific gravity being between 5.62 and 5.96.

It is a little heavier than selenium, but not quite so heavy as tellurium.

Under appropriate conditions metallic arsenic ex-

hibits great chemical activity. When it is volatilised it yields a vapour which burns with a faint blue flame, producing As_2O_3, arsenious acid. Powdered metallic arsenic takes fire spontaneously in chlorine gas, producing $AsCl_3$, the only known chloride of arsenic.

A mixture of one part of powdered metallic arsenic with three parts of powdered chlorate of potash forms a very dangerous explosive, which explodes most violently when struck with a hammer on an anvil. Such a mixture is dangerous to make, and should be made only on a very small scale, and with avoidance of friction.

Nitrates likewise make explosive mixtures with arsenic.

Metallic arsenic has no action on water or steam, but appears to combine with any oxygen that may be held in aqueous solution.

Dilute acids have little or no action, but boiling hydrochloric acid appears to dissolve it slowly (probably indirectly through the action of oxygen taken up from the atmosphere).

Concentrated sulphuric acid has no action in the cold, but is reduced to sulphurous acid and even to the condition of free sulphur on being boiled with metallic arsenic.

Nitric acid attacks metallic arsenic, yielding ultimately arsenic acid.

The common oils and fats are attacked by metallic arsenic when they are somewhat strongly heated with

it, giving a black liquid which becomes semi-solid on cooling.

When sulphur is melted with arsenic combination takes place, and various sulphurets are produced according to the proportions employed.

Almost every metal combines with metallic arsenic under the influence of heat, and forms compounds which are generally called alloys, some, however, being dignified as arseniurets or arsenides.

The general effect of arsenic upon a metal is to render it brittle and to lower its melting-point. The colour is often altered and whitened.

Mercury takes up much arsenic when it is boiled with arsenic, and forms a grey amalgam consisting of five parts of mercury and one part of arsenic.

Gold takes up one-sixtieth of its weight of arsenic, giving an alloy pale in colour, and brittle and much harder than gold.

Platinum alloys itself with arsenic, and the alloy of platinum with arsenic has played a useful part in the metallurgy of platinum. For that purpose, however, it is arsenious acid rather than metallic arsenic which is used.

Molten silver takes up as much as one-fourteenth of arsenic, forming a brittle yellow alloy.

The alloy of arsenic with copper, which is known as white copper or white tombac, has the composition Cu_2As, and may be prepared by heating together finely divided copper and arsenic.

An arseniuret or arsenide of iron having the composition FeAs has been obtained by heating together in a closed crucible a mixture of 54 parts of iron with 108 parts of metallic arsenic. This alloy was white and brittle, easily reduced to powder. It contained:—

Arsenic	75	63
Iron	56	37
	131	100

Bismuth, antimony, tin, zinc, and lead, each of these metals combines with arsenic, when metallic arsenic and the metal are heated together in closed vessels.

Heated with potassium or sodium metallic arsenic forms alloys which possess the property of decomposing water, acidulated if necessary, and yielding arseniuretted hydrogen by that decomposition.

Such alloys if they were heated in a current of dry air or oxygen would combine with the oxygen, at any rate, at temperatures bordering on redness; and arseniates would be the result.

The alloys of some of the heavy metals with arsenic are difficult of complete decomposition by heat. When heated to redness in the air they sometimes throw off part of the arsenic in the form of arsenious acid, but a portion of the arsenic remains behind in the form of an arseniate. By adopting the plan of fusing with nitre, the alloys of arsenic with heavy metals may be converted into a mixture

of arseniate of potash (which will dissolve in water on subsequent cooling), and oxide of the heavy metal, which will remain insoluble, and be separable from the alkaline arseniate in solution. By that means the analytical difficulty presented by some of these alloys may be surmounted.

Metallic arsenic has no tendency whatever to unite directly with carbon, although, as will be explained in the proper place, it has an especial and peculiar aptitude for entering into intimate organic relation with hydrocarbon radicals when the proper conditions are complied with. It is, however, worthy of mention that a case is on record where the charcoal furnished by an organic nitrogenous substance retained arsenic so obstinately that the existence of arsenic in the original organic compound was, for a long time, overlooked. Such an example of the concealment of the presence of arsenic was furnished by arseniate of rosaniline, the nature of which was not at first recognised. In that instance it was necessary to *burn up* the charcoal in a current of air or oxygen in order to obtain the arsenic in the form of arsenious acid.

Metallic arsenic is found in Nature in several mining districts in Saxony, Bohemia, and Transylvania; also in Norway and the United States of America.

It occurs much more abundantly in a state of combination with various metals and with sulphur. Its

commonest compounds are its combinations with iron, copper, nickel, cobalt, and with sulphur. There is no mining district in which arsenic is unknown, but it is especially abundant in Germany and in Spain, in the province of Catalonia. It is found in Cornwall in tolerable abundance. Pyrites contain more or less of it, and native sulphur is never quite free from it. Nearly every iron ore contains it in some shape or other, though the proportion is sometimes very small.

The actual proportion of arsenic in the earth's crust is no doubt very small, but traces of arsenic are found almost everywhere on the surface of this planet. In the mining districts it is discharged into the atmosphere by many metallurgical operations, even in the daily life in town and country it finds its way into the atmosphere, since wherever coal is burnt traces of arsenious acid are sent into the air. Every shower of rain washes arsenic out of the air and distributes it over the land or into the sea. Minute traces of arsenic are all-pervading, and, as a necessary consequence, the mere detection of arsenic is devoid of meaning unless it is, to some extent, a quantitative operation.

Section 2.—Arsenious and Arsenic Acids and their Salts.

There are two oxides of arsenic, viz. arsenious acid and arsenic acid. The first of these oxides is the

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"*Arsenic*" of commerce, white arsenic, as it is called. It is the volatile product of the roasting of the various ores of arsenic, and its production has been described by an old writer in these words: "The ore is thrown into a furnace resembling a baker's oven, with a flue or horizontal chimney nearly two hundred yards long, into which the fumes pass, and are condensed into a greyish or blackish powder. This is refined by a second sublimation in enclosed vessels with a little potash to detain impurities." The finished product is a heavy white solid with the following percentage composition:—

Arsenic	75.76
Oxygen	24.24
	100.00

Its chemical formula is As_2O_3, and it is a mixture of the two or three *allotropic* varieties of arsenious acid. There is the vitreous variety, which is amorphous and quite distinct from the crystalline variety; but the different varieties pass into one another with great facility, and whether one or another form predominates in a mass of arsenious acid depends upon slight alterations in the physical conditions. Arsenious acid volatilises at about 218° Centigrade, giving a colourless vapour which, if it be allowed to condense very gradually at a temperature only a few degrees below 218°, passes through a condition of partial fusion before it assumes the completely solid state, and under these

physical conditions becomes the vitreous or amorphous variety of arsenious acid.

The crystalline variety is obtained by allowing the vapours to condense in contact with surfaces cooled much below 218°, under conditions where there can be no partial fusion of the sublimate.

The amorphous arsenious acid is much heavier than the crystalline variety; its specific gravity is 3.7385, whilst the crystals have a specific gravity of 2.695.

The solubility of the different arsenious acids varies considerably, especially in cold water. A boiling saturated solution of arsenious acid contains some eight or ten grammes of arsenious acid in 100 c. c. of the solution, and on cooling deposits crystals of arsenious acid, leaving a cold saturated solution containing 3.3 grammes in the 100 c. c. of cold solution. But when the attempt is made to obtain a cold saturated solution without a preliminary preparation of the hot solution, when excess of finely powdered arsenious acid is persistently shaken up with cold water, then only one-tenth of that quantity of As_2O_3 passes into solution; and under those conditions only 0.3 gramme of As_2O_3 is found in 100 c. c. of the cold solution.

The following experiment is very instructive. Take one gramme of finely powdered As_2O_3 and shake it up with one litre of cold distilled water, and note how slowly the substance dissolves, and that in no reasonable time, and that with no reasonable persistence in shaking up is it possible to induce the whole of the

gramme or nearly the whole of the gramme to enter into solution. The results of such experiments appear to indicate that there is a variety of As_2O_3 which is almost insoluble in cold water.

In boiling dilute hydrochloric acid As_2O_3 dissolves more readily than in boiling water, and on cooling As_2O_3 separates out of solution uncombined either with water or with HCl.

This property of separating out of solution in the anhydrous condition is one of the points of distinction between arsenious acid and the other oxide of arsenic, viz. arsenic acid, which enters into real combination with water producing hydrates, and can only be deprived of its combined water by the employment of considerable heat.

Sulphuretted hydrogen gas transforms As_2O_3 into the yellow sulphuret of arsenic As_2S_3 thus:—

$$3H_2S + As_2O_3 = 3H_2O + As_2S_3.$$

In order that the separation of the yellow sulphuret may be complete it is advisable to make an addition of an excess of dilute hydrochloric acid, and under that condition the precipitation of the sulphuret of arsenic is absolute. The yellow sulphuret is constant in composition, and is one of the most characteristic compounds of arsenic. It is one of the forms in which arsenic is weighed in performing a quantitative estimation of arsenic. It is the sulphur representative of arsenious acid, and dissolves with great ease in

ammonia, or carbonate of ammonia, or sulphuret of ammonia, from which solutions it may be reprecipitated by the addition of hydrochloric acid.

Arsenious acid is one of the weakest acids. Its aqueous solution reddens litmus feebly, but on the other hand, although it dissolves freely in solutions of alkaline carbonates, it does not drive out the carbonic acid at ordinary temperatures. It dissolves in excess of caustic potash or soda, but it does not neutralise the alkali, and even the carbonic acid of the air drives out the arsenious acid, which in course of time separates out in the form of crystals.

In solution of ammonia it dissolves more readily than in water devoid of ammonia, but the ammonia passes off when the water evaporates, and nothing but As_2O_3 remains behind as a residue. Excess of the acid forms soluble acid salts with lime, strontia, or baryta, and solutions of these acid-salts give basic precipitates when lime-water, strontia-water, or baryta-water is added in excess.

The arsenite of copper $2CuO,As_2O_3$ (Scheele's green) is a very well-known substance. It is formed on mixing together an aqueous solution of arsenious acid with solution of ammonio-sulphate of copper, when a *brilliant yellow green* precipitate falls down. This precipitate is very soluble either in ammonia or acids; and, of course, would only make its appearance in the absence of excess of ammonia or acid.

The arsenite of silver $2Ag_2O,As_2O_3$ forms a very

characteristic precipitate when ammonio-nitrate of silver and the acid are brought together. The colour of this silver precipitate is canary yellow. Like the copper precipitate just mentioned it is very sensitive to excess of ammonia or of acid, which has to be carefully guarded against in order to avoid failure.

Recently precipitated hydrated peroxide of iron, when added in great excess, possesses the property of removing arsenious acid from its aqueous solution with great completeness. For this purpose the amount of the iron precipitate is required to be *ten times* the weight of the arsenious acid; and in this calculation the iron is to be reckoned as anhydrous peroxide. So thorough is the action, and so little objectionable is the agent, that Bunsen and Berthold have recommended the use of it as an antidote in cases of arsenical poisoning when the poisoning is quite recent. One of the best forms of the remedy is the use of a strong solution of ferric chloride mixed with calcined magnesia in excess.

Arsenious acid is interesting inasmuch as it is one of the most stable forms of arsenic. As has been mentioned, this is the form which arsenic assumes when the ores of arsenic are roasted in contact with the atmosphere. It is also the only form which arsenic takes when metallic arsenic is heated in excess of air. Even the other oxide of arsenic, viz. As_2O_5, arsenic acid, is resolved into As_2O_3 and free oxygen when a high red heat is reached. The conditions being—pre-

sence of excess of oxygen, high red heat, and *absence* of alkali, or powerful basic substances, the sole form taken by arsenic is As_2O_3, arsenious acid.

When, however, the last condition is not complied with, and when there is excess of alkali or powerful basic substance, then the stable form is the other oxide of arsenic, viz. As_2O_5 arsenic acid, which in that case enters into combination and yields an arseniate of the alkali or strongly basic substance. Under these conditions arsenites take up oxygen and become arseniates. And, when there is no free oxygen to be taken up, then the arsenious acid, so to speak, feeds upon itself, and five molecules of it are resolved into three molecules of arsenic acid and four atoms of metallic arsenic, according to this equation :—

$$5As_2O_3 = 3As_2O_5 + As_4.$$

"Dr. Wollaston first observed, that when a mixture of arsenious acid with quicklime is heated in a glass tube, at a certain temperature ignition suddenly pervades the mass and metallic arsenic sublimes."

If then some of the arsenious acid in contact with strong bases, at a high red heat, acts towards itself as a reducing agent and evolves metallic arsenic, one would anticipate that the presence of a highly reducing agent, such as charcoal, should bring about complete reduction of the whole of the arsenic, and that expectation is thoroughly borne out by experiment. And one of the most characteristic reactions of arsenious acid is the production of the *arsenical mirror*

by reduction of that substance by red-hot charcoal, which is so placed in a narrow tube of hard glass that the volatilised arsenious acid is compelled to come into contact with it and undergo reduction, and deposit a shining ring of metallic arsenic in the cooler part of the tube.

Arsenic acid, sometimes called arsenic oxide, or arsenic pentoxide, or arsenic anhydride, is the only other compound of arsenic with oxygen. Its formula is As_2O_5. It cannot be obtained from arsenious acid by simply heating that substance in contact with atmospheric air or oxygen. At very elevated temperatures arsenic acid is indeed split up into arsenious acid and free oxygen. Arsenic acid is obtainable from arsenious acid by several roundabout operations.

As has been mentioned the admixture of quicklime with arsenious acid brings about a very remarkable decomposition when the materials are strongly heated; and under those conditions 60 per cent. of the arsenic in the arsenious acid passes into the condition of the higher acid of arsenic, and 40 per cent. of the arsenic sublimes in the condition of metallic arsenics. In this instance the process is a furnace operation, and the acid forms a compound with the lime.

The usual method resorted to in order to convert arsenious into arsenic acid is to boil it with nitric acid or with a mixture of nitric and hydrochloric acids. In that manner an aqueous solution of the *hydrate*

of arsenic acid is produced. By evaporating by the application of heat, the water is driven off and there remains a white concrete substance differing in many respects from arsenious acid. This residue is arsenic acid. Its specific gravity is 3.391. It is not crystalline. It is fixed in the fire (at anyrate at a low red heat), whereas arsenious acid volatilises at about 218° Centigrade. Its composition is:—

Arsenic	65.2
Oxygen	34.8
	100.0

If the cooled mass be placed in contact with water in excess it will enter into chemical composition with water, giving the tri-hydrate $As_2O_5,3H_2O$, which is sometimes written thus, H_3AsO_4, the formula being halved.

The aqueous solution of this hydrate is very strongly acid, and is strikingly different from the aqueous solution of arsenious acid.

There is a very close and far-reaching resemblance between arsenic and phosphoric acid. Just as there are three different hydrates of phosphoric acid, so there are three corresponding hydrates of arsenic acid; but the hydrates of arsenic acid pass more readily into each other than in the case of phosphoric acid. And simple solution in water resolves both of the other hydrates of arsenic acid into the tri-hydrate.

The salts formed by arsenic acid with the alkalis

are soluble in water. The salts of baryta, strontia, and lime are all of them soluble in excess of acid. The acid salts are soluble but the basic salts are insoluble in water. In presence of ammoniacal salts the basic salts of baryta, strontia, and lime become soluble.

There is an ammonia arseniate of magnesia which is a very close representative of the corresponding phosphate, and which is admirably adapted for quantitative employment. Its formula is $As_2O_5(MgO)_2(NH_4)_2O + 12H_2O$. It is crystalline, very insoluble in strongly ammoniacal liquids, just as the corresponding phosphate.

The arseniate of silver, which is brick red in colour, is a very characteristic arsenical compound. It is obtained by mixing solution of arsenic acid with ammonio-nitrate of silver. For this purpose the ammonio-nitrate of silver must be very carefully prepared—only *just* enough ammonia being added to barely dissolve the precipitate given on the first addition of drops of ammonia to the nitrate. Excess either of acid or of ammonia redissolves this precipitate. The formula of the precipitate is Ag_3AsO_4.

There is also a precipitate when solutions of sulphate of copper and arsenic acid are brought together and very carefully dosed with very dilute ammonia. This precipitate has the formula $HCuAsO_4$ and is blue-green in colour, and is soluble in slight excess, either of ammonia or nitric acid.

Just as phosphoric acid forms a most insoluble yellow precipitate with molybdate of ammonia in presence of much nitric acid and nitrate of ammonia, so likewise does arsenic acid.

This test is especially applicable when very small quantities of arsenic acid or its salts are required to be tested for the presence of arsenic acid.

It is essential that the molybdate of ammonia be added in excess, and that excess of nitric acid be present, and the mixture should be warmed. These conditions having been complied with the presence of arsenic acid, or its salts, will be announced by the appearance of a yellow colour in the solution, and, if more than a trace of arsenic acid be there, a yellow precipitate of the arsenio-molybdate of ammonia will, by-and-by, settle down. Of course it will be understood that a testing, of this kind, for arsenic acid is valid only in the absence of phosphoric acid.

The appropriate solution of molybdate of ammonia is prepared by dissolving one part of molybdic acid in eight parts of strong ammonia, and then adding twenty parts of nitric acid. Forty times as much molybdic acid must be used in order to precipitate a given quantity of arsenic acid.

The behaviour of arsenic acid and the salts of arsenic acid towards sulphuretted hydrogen differs somewhat from that of arsenious acid towards that reagent. The solution of arsenic acid, or arseniate having been acidified by means of dilute hydrochloric acid, sulphuretted

hydrogen gas may be passed into the liquid, when the following may be noted. In the cold, at ordinary temperatures, the action of the gas is exceedingly slow, twenty-four hours being required to complete the production of the yellow sulphuret As_2S_3; but, if the liquid be warmed up to 60° or 70° Centigrade, then the production of the yellow sulphuret is almost immediate.

The equation expressing the chemical reaction is:—

$$5H_2S + As_2O_5 = 5H_2O + As_2S_3 + S_2,$$

and, as will be perceived, there is production of sulphur in addition to the yellow sulphuret As_2S_3.

Instead of directly passing the sulphuretted hydrogen through a heated solution of arsenic acid it will be found convenient to employ sulphurous acid, and, in that way, reduce the arsenic acid into arsenious acid before resorting to sulphuretted hydrogen. The chemical change may be expressed thus:—

$$As_2O_5 + 2SO_2 = As_2O_3 + 2SO_3.$$

Of course the $2SO_3$ acts upon water and becomes $2(SO_3H_2O)$. The solution should be warmed in order to facilitate the chemical change.

Section 3.—*The Chloride and the Hydride of Arsenic.*

Chloride of arsenic, formula $AsCl_3$, theoretical vapour-density = 6.289. Dumas found 6.300. It is a heavy colourless liquid, which decomposes water when brought into contact with water. Its boiling-

point is 132° Centigrade. It is produced by distilling a mixture of common salt and arsenious acid with excess of sulphuric acid, and is a highly poisonous liquid which fumes in moist air owing to the action of its vapour on moisture. There is no pentachloride of arsenic.

Bromine and iodine form corresponding compounds. The iodide AsI_3 is a beautiful substance described as an orange-coloured sublimate. It is prepared by heating a mixture of iodine and metallic arsenic. It is very soluble in hot water, and, curiously enough, such a solution when boiled down to dryness leaves a residue of iodide of arsenic.

The hydride of arsenic, also called arseniuretted hydrogen, AsH_3, is a colourless gas, produced in carrying out the celebrated Marsh test for arsenic, but, in that instance, it is mixed with a large volume of hydrogen gas. It has not often been prepared in a state of even approximate purity. In anything like a state of purity it is terribly poisonous—said to be the most poisonous substance known.

Its vapour-density, according to Dumas, is 2.695, which agrees very closely with the usual formula assigned to it. The extremely poisonous nature of this compound renders it very dangerous, and has no doubt hindered investigation.

AsH_3 is the chemical representative of ammonia NH_3, and on that account very interesting to the chemist. In a state of purity—unaccompanied by hydrogen—it was obtained, by Soubeiran, by the

action of strong hydrochloric acid upon an alloy of arsenic and zinc, in which the arsenic was in excess over the zinc. Such an alloy Soubeiran procured by fusing a mixture of equal weights of arsenic and granulated zinc; and, using that alloy, Soubeiran obtained arseniuretted hydrogen which dissolved in a saturated aqueous solution of sulphate of copper, and left no residue of unabsorbed hydrogen. The gas has a most disagreeable smell, like garlic. Unlike ammonia, which dissolves in water to an enormous extent, arseniuretted hydrogen is only slightly soluble in water; 100 volumes of water dissolving only about 20 volumes of AsH_3. Furthermore, it should be borne in mind that arseniuretted hydrogen has no tendency to combine with hydrochloric acid—in that respect, too, being utterly different from ammonia. It is like ammonia in its passiveness in relation to the alkalis.

Its chemical activity is that of a most powerful and most peculiar reducing agent, and the action is, as a rule, rapid and apparently instantaneous. The common solutions of gold, platinum, and silver are, at once, decomposed by this gas, the metal being precipitated whilst the arsenic in the arseniuretted hydrogen suffers oxidation and enters into solution in place of the noble metal which is assuming the metallic state.

With solution of sulphate of copper there is, as has been mentioned, a very peculiar action, and a precipitate is formed; but the precipitate does not consist of metallic copper but of an alloy of arsenic with copper.

With solution of acetate of lead acidulated with acetic acid there is no visible action on bringing the gas into contact with it: which distinguishes the gas from sulphuretted hydrogen.

Section 4.—Organo-Metallic Compounds of Arsenic.

In the year 1760 a very extraordinary liquid possessing the property of taking fire spontaneously on exposure to the air was discovered by Cadet. The liquid became known as Cadet's fuming liquor or alcarsin, and the study of it by the great German chemist, Bunsen, rather more than seventy years later, laid the foundation of much that is embraced by modern organic chemistry.

Cadet's fuming liquor is produced by the careful distillation, at moderately high temperatures, in a retort, of an intimate mixture of powdered arsenious acid and dry acetate of potash.

In that experiment, instead of a simple reduction of the arsenious acid so as to yield a sublimate of metallic arsenic, there was also produced a new and strange organic liquid containing arsenic in intimate union with the hydro-carbon radical methyl. Bunsen's work established the real nature of Cadet's fuming liquor; and, inasmuch as this compound of arsenic with methyl was the first recognised compound of any metal or semi-metal with any hydro-carbon radical, Bunsen is justly held to be the discoverer of this

class of chemical substances. Organo-metallic compounds, as possible existences, were discovered when Bunsen recognised kakodyl in Cadet's fuming liquor. At the time of Bunsen's great investigation (beginning with the year 1837 and ending with the year 1842) the now familiar notion that acetates contain the organic radical methyl, as an integral part of the acetic acid, had not presented itself to the minds of chemists, and the explanation of the production of such a substance as Bunsen's kakodyl by such an operation as the action of arsenious acid on acetate of potash was much more difficult than it is in the light of to-day's chemistry.

The chemical change taking place when arsenious acid is distilled in contact with dry acetate of potash may be formulated thus:—

4 Molecules of Acetate of Potash.

$KOCOCH_3$
$KOCOCH_3$
$KOCOCH_3$
$KOCOCH_3$

$+$

One Molecule of Arsenious Acid.

As_2O_3

$=$

$KOCOO$
$KOCO$
$KOCOO$
$KOCO$

$+$

Oxide of Kakodyl.

$As_2(CH_3)_4O$

$=$

Neutral Carbonate of Potash. $2K_2CO_3$ $+$ Carbonic Acid. $2CO_2$ $+$ Alkarsin or Oxide of Kakodyl. $As_2(CH_3)_4O$.

This equation requires that 392.4 parts of acetate of potash should be taken along with 198 parts arsenious acid, being about double as much potash salt as arsenious acid. Bunsen used equal proportions of acetate and the acid; that is to say, the acid was in great excess, which no doubt occasioned destructive oxidation of some of the alkarsin with separation of metallic arsenic and formation of water, acetone, and acetic acid.

The yield of crude alkarsin from the distillation of 100 parts of arsenious acid and 100 parts of acetate of potash is recorded as 30 parts, which indicates that about one-half of the methyl in the acetate of potash originally taken had survived so as to form the ultimate arsenical organo-metallic liquid.

The product which distilled over is recorded as consisting of an upper aqueous layer containing water, acetone, and acetic acid, and a lower oleaginous layer not miscible with the aqueous layer, and some solid metallic arsenic at the bottom of all. The evolution of abundance of carbonic acid during the distillation, and the finding of the carbonate of potash in the residue in the retort have likewise been duly recorded.

The important product is the heavy oily liquid —the fuming liquor of Cadet, which Bunsen most carefully washed, dried, and distilled in a current of hydrogen gas, so as to avoid any oxidation from the atmosphere.

This liquid was found to consist mainly of oxide of

kakodyl, $As_2(CH_3)_4O$, but contained a little free kakodyl, $As_2(CH_3)_4$, which rendered it spontaneously inflammable in contact with the air.

Taking this liquid as his starting-point, Bunsen carried out the celebrated research which disclosed the existence of kakodyl and the compounds and derivatives of kakodyl, opened up wide fields of undreamt of chemistry, and imparted a degree of certainty and precision to the initial stages of organic chemistry the influence of which has been felt up to the present time.

When kakodyl was discovered organic chemistry was very young, and though chemists had visions of new organic radicals (cyanogen, for instance, had been discovered by Gay-Lussac in 1815), the notion of atomicity and organic types and series was undeveloped; and kakodyl and its compounds and derivatives wore a dress somewhat different from that which they would have assumed if they had been discovered within the last few years. The following are some members of the kakodyl series:—

Oxide of kakodyl . .	$As_2(CH_3)_4O = As(CH_3)_2\ As(CH_3)_2O$
Radical kakodyl . .	$As_2(CH_3)_4 = As(CH_3)_2\ As(CH_3)_2$
Chloride of kakodyl .	$As(CH_3)_2Cl$
Trichloride of kakodyl	$As(CH_3)_2Cl_3$
Kakodylic acid. . .	$As(CH_3)_2OOH$

Kakodyl, $As_2C_4H_{12} = As(CH_3)_2\ As(CH_3)_2$, the radical of the series, which, in times gone by, was described as being "the most perfect type of an organic quasi-

metal which chemistry yet possesses," is obtained from Cadet's fuming liquor by heating it with strong hydrochloric acid, which converts that liquid mainly into chloride of kakodyl, and then decomposing the chloride, which is an oily product, by means of metallic zinc, which gives a solid compound of chloride of zinc with kakodyl. Treatment of this solid compound with water gives solution of chloride of zinc and free kakodyl.

It is a colourless, transparent, thin liquid, heavier than water, and non-miscible with and almost absolutely insoluble in water. It dissolves readily in alcohol and ether.

Its boiling-point is about 170° Centigrade, and it solidifies at 6° Centigrade, crystallising in large transparent square prisms.

It possesses a most peculiar and offensive smell, and its vapours are exceedingly poisonous. It takes fire spontaneously on exposure to the air, and should be kept either in hermetically sealed vessels or else under water carefully freed from air by previously boiling.

In contact with chlorine gas it takes fire, and then there is irregular and destructive chemical action; but when the chlorine is dissolved in water, so as to moderate the action, then the chemical change is quite regular, thus :—

$$\left.\begin{matrix}\text{As}(CH_3)_2 \\ \text{As}(CH_3)_2\end{matrix}\right\} + Cl_2 = 2\text{As}(CH_3)_2Cl.$$

Kakodyl. Chloride of Kakodyl.

With bromine and iodine there are parallel reactions.

Kakodyl dissolves sulphur and combines with it, producing sulphuret of kakodyl.

When air is slowly admitted to kakodyl oxygen is taken up by the kakodyl and the oxide formed thus :—

$$\text{Kakodyl.} \qquad\qquad \text{Alkarsin.}$$
$$2\begin{Bmatrix}\mathrm{As(CH_3)_2}\\ \mathrm{As(CH_3)_2}\end{Bmatrix} + \mathrm{O_2} = 2\mathrm{As_2(CH_3)_4\,O},$$

and by the further action of the atmosphere kakodylic acid is slowly produced.

Kakodyl, kept in sealed vessels, out of contact with the air, is a very stable body. It may be considerably heated without decomposition, but, at about 400° Centigrade, it is resolved into metallic arsenic and a mixture of marsh gas and olefiant gas, thus :—

$$\mathrm{As_2(CH_3)_4} = \mathrm{As_2} + 2\mathrm{CH_4} + \mathrm{C_2H_4}$$

and there is no deposit of carbon.

Kakodyl has a vapour density of 7.101 as found by Bunsen's experiment. The theory requires 7.27 for the formula $\mathrm{As_2C_4H_{12}}$. Its percentage composition is :—

		Theory.
$\mathrm{As_2}$	150	71.43
$\mathrm{C_4}$	48	22.86
$\mathrm{H_{12}}$	12	5.71
	210	100.00

Although this substance contains as much as 71 per cent. of arsenic, none of the ordinary tests for arsenic reveal the presence of arsenic in it, except such tests as involve raising it to temperatures bordering on low red heat. Sulphuretted hydrogen does not give the yellow sulphuret of arsenic, zinc and hydrochloric acid do not give arseniuretted hydrogen. It is a typical organo-metallic compound, the union of the arsenic with the carbon or hydro-carbon being so complete that the whole group AsC_2H_4 behaves like an atom of hydrogen, forming an organic quasi-metal.

Since the time of the kakodyl-research the chemistry of organo-metallic bodies has been greatly extended, and the arsenical examples have been greatly multiplied.

Cahours and Riche have, for instance, obtained arsentrimethyl, $As(CH_3)_3$, a liquid boiling at 120° Centigrade; and Baeyer has also added to the number, and brought beautiful order into the chemistry, of these arsenical organo-metallic substances.

Section 5.—*Kakodylic Acid and its Salts.*

Kakodylic acid, upon which great expectations are founded, $AsC_2H_7O_2 = As(CH_3)_2OOH$, is prepared by oxidising kakodyl, or its oxide alkarsin, by means of peroxide of mercury in contact with water.

The action is very energetic, and care must be taken to avoid too great heating of the materials. An excess of peroxide of mercury is placed in water in a flask

which is kept cool by being immersed in cold water. Then the kakodyl or alkarsin is carefully added, being run in under water. By suitable agitation, and by the external application of cold water to the flask, the chemical action is kept under proper control. The first product is kakodylate of mercury and metallic mercury, thus :—

$$As_2(CH_3)_4 + 4HgO = As_2(CH_3)_4O_4Hg + Hg_3.$$

Then more kakodyl is carefully added to decompose the kakodylate of mercury so long as metallic mercury is caused to separate, and until a slight smell of kakodyl becomes perceptible. The kakodylic acid dissolves in the water, and its solution may be evaporated down and the residue dissolved in alcohol, from which it crystallises beautifully in large colourless crystals. It is not so soluble in alcohol as in water, and in ether it is quite insoluble.

The yield of the acid is good. From 76 grammes of Cadet's fuming liquor Bunsen obtained 88 grammes of kakodylic acid. The theoretical yield from 76 grammes of oxide of kakodyl, $As_2(CH_3)_4O$, is 92.8 grammes of the acid.

The stability of kakodylic acid is wonderful. Nitric acid does not attack it, nor yet sulphuric acid mixed with chromate of potash. It is not reduced by sulphurous acid, nor by oxalic acid, nor by ferrous salts. But phosphorous acid, acidulated stannous solution, or zinc act upon it, and kakodyl is produced.

Dry hydriodic acid reduces it thus :—

$$AsC_2H_7O_2 + 3HI = AsC_2H_6I + 2H_2O + I_2.$$

Sulphuretted hydrogen, either in a dry condition or dissolved in water, attacks kakodylic acid with vigour, developing heat and producing bisulphuret of kakodyl

$$2AsC_2H_7O_2 + 3H_2S = AsC_2H_6AsC_2H_6S_2 + S + 4H_2O.$$

If weak alcohol be taken instead of water, the reaction is slightly different, thus :—

$$2AsC_2H_7O_2 + 3H_2S = AsC_2H_6AsC_2H_6S + S_2 + 4H_2O.$$

Kakodylic acid has furnished the following on being analysed :—

		Calculated.
C_2 . . .	24	17.39
H_7 . . .	7	5.07
As . . .	75	54.35
O_2 . . .	32	23.19
	138	100.00

The salts of kakodylic acid are as a rule very soluble in water. They seldom crystallise, and on evaporating down their solutions in water they form gummy masses.

According to Laurent the ammonia-salt does not exist. The potash-salt is very deliquescent. The soda-salt is less deliquescent, and has been made on a considerable scale for medicinal use.

Kakodylic acid forms crystalline compounds with hydrofluoric and hydrochloric acids. The compound with hydrochloric acid, $AsC_2H_7O_2HCl$, is prepared by dissolving kakodylic acid in strong hydrochloric acid and leaving the solution *in vacuo*. It forms a mass of crystals, and is without smell, but very acid to the taste. Water resolves it into hydrochloric acid and kakodylic acid.

CHAPTER II.

DETECTION AND MEASUREMENT OF ARSENIC.

Section 1.—*Marsh's Test.*

THE Marsh's test, named after Marsh, who discovered it, occupies a unique position in arsenical testing owing to its surpassing delicacy and *almost* absolute applicability. The qualification "*almost*" is called for by reason of the existence and importance of the instances wherein arsenic has entered into organo-metallic relations with the organic elements and rendered itself irresponsive to most of the general tests for arsenic.

The justly celebrated James Marsh, chemist in the Arsenal at Woolwich, and also chemical assistant at the military school under Faraday, was born about the year 1790, and died at Woolwich, 21st June 1846. His discovery of the famous Marsh's test was brought before the Society of Arts in London and published in Jameson's *New Edinburgh Philosophical Journal*, vol. xxi., in the year 1836.

The author of this treatise—bearing in mind the current ignorance, and the disparagement of this process, and the misapprehension which is rife—re-

publishes Marsh's own words, quoting them from the journal just mentioned.

"*Account of a Method of separating small quantities of Arsenic from substances with which it may be mixed, by* JAMES MARSH, Esq., *of the Royal Arsenal, Woolwich (communicated to the Society of Arts of London).*

"Notwithstanding the improved methods that have of late been invented of detecting the presence of small quantities of arsenic in the food, in the contents of the stomach, and mixed with various other vegetable and animal matters, a process was still wanting for separating it expeditiously and commodiously, and presenting it in a pure unequivocal form for examination by the appropriate tests. Such a process should be capable of detecting arsenic not only in its usual state of white arsenic or arsenious acid, but likewise in that of arsenic acid and of all the compound salts formed by the union of either of these acids with alkaline substances.

"It ought also to exhibit the arsenic in its reguline or metallic state free from the ambiguity which is sometimes caused by the use of carbonaceous reducing fluxes. It appeared to me that these objects might be attained by presenting to the arsenic hydrogen gas in its nascent state, the first action of which would be to deoxygenate the arsenic; and the next to combine with the arsenic thus deoxygenated into

the well-known gas called arseniuretted hydrogen. Being thus brought to the gaseous state the arsenic would spontaneously (so to speak) separate itself from the liquor in which it was before dissolved, and might be collected for examination by means of any common gas apparatus, thus avoiding the trouble, difficulty, and ambiguity of clarification and other processes whereby liquors suspected of containing arsenic are prepared for the exhibition of the usual tests, or of evaporation and deflagration which are sometimes had recourse to in order to separate the arsenic from the organic substances with which it may have been mixed. I had the satisfaction of finding on trial that my anticipations were realised, and that I was thus able not only to separate very minute quantities of arsenic from gruel, soup, porter, coffee, and other alimentary liquors, but that by continuing the process a sufficient length of time I could eliminate the whole of the arsenic in the state of arseniuretted hydrogen, either pure or at most only mixed with an excess of hydrogen.

"If this gas be set fire to as it issues from the end of a jet of fine bore into the common air the hydrogen, as the more combustible ingredient, will burn first, and will produce aqueous vapour, while the arsenic will be deposited either in the metallic state or in that of arsenious acid, according as it is exposed partially or freely to the air. The former condition is brought about by holding a piece of cold window-glass opposite

to and in contact with the flame, when a thin metallic film will be immediately deposited on its surface; and the latter by receiving the flame within a glass tube open at both ends, which in half a minute will be found to be dimmed by a white pulverulent sublimate of arsenious acid. By directing the flame obliquely upon the inside of the tube it strikes against the glass and deposits the arsenic partly in the metallic state. In this case, if the tube while still warm be held to the nose, that peculiar odour somewhat resembling garlic which is one of the characteristic tests of arsenic will be perceived. Arseniuretted hydrogen itself has precisely the same colour, but considerable caution should be used in smelling it, as every cubic inch contains about a quarter of a grain of arsenic.

The requisite apparatus is as simple as possible, being—

"A glass tube open at both ends and about three-quarters of an inch in its internal diameter. It is bent in the form of a syphon (*a a*), the shorter leg being about 5 inches and the longer leg about 8 inches in length. A stopcock (*b*) ending in a jet of fine bore passes tightly through a hole made in the axis of a soft and sound cork, which fits airtight into the opening of the lower bend of the tube, may be further secured, if requisite, by a little common lute. To fix the apparatus, when in use, in the upright position a hole is made in the wooden block *c* for the reception of the pillar *d*, and a groove is cut in the top of the same block to

receive the bend of the tube *a a*. Two elastic slips (*e e*) cut from the neck of a common bottle of india-rubber keep the tube firm in its place.

"The matter to be submitted to examination and supposed to contain arsenic, if not in the fluid state, such as pastry, pudding, or bread, &c., must be boiled with two or three fluid ounces of clean water for a sufficient length of time. The mixture so obtained must then be thrown in a filter to separate the more solid parts; thick soup or the contents of the stomach may be diluted with water and also filtered; but water, gruel, wine, spirits, or any kind of malt liquor, and such like as tea, coffee, cocoa, &c., can be operated on without any previous process.

"When the apparatus is to be used a bit of glass rod about an inch long is to be dropped into the shorter leg, and this is to be followed by a piece of clean sheet-zinc about an inch and a half long and half an inch wide, bent double so that it will run down the tube till it is stopped by the piece of glass rod first put in. The stopcock and jet are now to be inserted and the handle is to be turned so as to leave the cock open. The fluid to be examined having been previously mixed with from a drachm and a half to three drachms of dilute sulphuric acid (1 acid and 7 water), is to be poured into the long leg till it stands in the short one about a quarter of an inch below the bottom of the cork. Bubbles of gas will soon be seen to rise from the zinc which are pure hydrogen if no arsenic be present;

but if the liquor holds arsenic in any form in solution the gas will be arseniuretted hydrogen. The first portions are to be allowed to escape in order that they may carry with them the small quantity of common air left in the apparatus; after which the cock is to be closed, and the gas will be found to accumulate in the shorter leg, driving the fluid up the longer one till the liquor has descended in the short leg below the piece of zinc, when all further production of gas will cease. There is thus obtained a portion of gas subject to the pressure of a column of fluid of from seven to eight inches high; when therefore the stopcock is opened the gas will be propelled with some force through the jet, and on igniting it as it issues (which must be done quickly by an assistant), and then holding horizontally a piece of crown or window glass over it in such a manner as to retard slightly the combustion, the arsenic (if any be present) will be found deposited in the metallic state on the glass, the oxygen of the atmosphere being employed in oxidising the hydrogen only during the process. If no arsenic be present then the jet of the flame as it issues has a very different appearance; and, although the glass becomes dulled in the first instance by the deposition of the newly formed water, yet such is the heat produced that in a few seconds it becomes perfectly clear and frequently flies to pieces.

"If the object be to obtain the arsenic in form of arsenious acid or white arsenic then a glass tube from

a quarter to half an inch in diameter (or according to the size of the jet of flame) and eight or ten inches in length is to be held vertically over the burning jet of gas in such a manner that the gas may undergo perfect combustion, and that the arsenic combined with it may become sufficiently oxidised; the tube will thus with proper care become lined with arsenious acid in proportion to the quantity originally contained in the mixture.

"When the glass tube is held at an angle of about 45° over the jet of flame three very good indications of the presence of arsenic may be obtained at one operation, viz. metallic arsenic will be found deposited in the tube at the part nearest where the flame impinges—white arsenic or arsenious acid at a short distance from it—and the garlic smell can be readily detected at either end of the tube in which the experiment has been made.

"As the gas produced during the operation is consumed the acid mixture falls into the short limb of the tube, and is thus again brought into contact with the zinc, in consequence of which a fresh supply is soon obtained. This gas, if submitted to either of the processes before described, will give fresh indications of the presence of the arsenic which the mixture may have originally contained, and it will be easily perceived that the process may be repeated as often as may be required at the will of the operator till no further proofs can be obtained.

"When certain mixed or compound liquors are operated on in the apparatus a great quantity of froth is thrown up into the tube, which may cause a little embarrassment by choking the jet. I have found this effect to take place most with the contents of the stomach, with wine, porter, tea, coffee, or soup, and indeed with all mucilaginous and albuminous mixtures. The means I adopt to prevent this effect from taking place, or at least for checking it in a great measure, is to grease or oil the interior of the short limb of the apparatus before introducing the substance to be examined, or to put a few drops of alcohol or sweet oil on its surface previously to introducing the stopcock and its appendages. I have however found, if the tube be ever so full of froth in the first instance, that in an hour or two if left to itself the bubbles burst, and the interior of the tube becomes clear without at all affecting the results.

"In cases where only a small quantity of the matter to be examined can be obtained, I have found a great convenience in using the small glass bucket *g*. Under such circumstances the bent glass tube may be filled up to within an inch of the short end with common water, so as to allow room for the glass bucket, which must be attached to the cork *c* by means of a little platina wire. A bit or two of zinc is to be dropped into the bucket with a small portion of the matter to be examined, and three or four drops of diluted sul-

phuric acid (acid 2, water 14), and the whole is then to be introduced into the mouth of the short limb of the tube. The production of gas under this arrangement is much slower, and of course requires more time to fill the tube than in the former case, but the mode of operating is precisely the same. Indeed it is of great advantage, when the quantity of arsenic present is very minute, not to allow the hydrogen to be evolved too quickly, in order to give it time to take up the arsenic. A slender glass funnel will be found of service when as much as a table-spoonful or even a teaspoonful of matter can be obtained for examination. In this case the tube is to be partly filled with common water, leaving a sufficient space for the substance to be examined; a piece of zinc is to be suspended from the cork by a thread or wire so as to hang in the axis of the tube, and the fluid to be operated on having been previously mixed with dilute sulphuric acid, is then to be poured through the funnel carefully, so as to surround the zinc, avoiding as far as possible to mix it with the water below, and the stopcock and its appendages are to be replaced in the mouth of the tube. The production of the gas then goes on as before stated, and the mode of manipulating with it is exactly the same as described in the foregoing part of the paper. It will be necessary for me in this place to explain the methods I employ after each operation to determine the integrity of the instrument, so as to satisfy myself that no arsenic remains adhering to the

inside of the tube or to the cork and its appendages before I employ it in another operation. After washing the apparatus with clean water a piece of zinc may be dropped in, and the tube filled to within half an inch of the top of the short limb; two drachms of diluted sulphuric acid are then poured in, and the stopcock and cork secured in its place. Hydrogen gas will in this case, as before, be liberated and fill the tube. If the gas as it issues from the jet be then inflamed and a piece of window-glass held over it as before described, and any arsenic remains, it will be rendered evident by being deposited on that glass; if so, this operation must be repeated till the glass remains perfectly clean after having been exposed to the action of the gas.

"When I have had an opportunity of working with so large a quantity of mixture as from two to four pints (imperial measure) I then have employed the instrument here figured, which is indeed but a slight modification of one of the instantaneous light apparatuses now well known and used for obtaining fire by the aid of a stream of hydrogen gas thrown on spongy platinum. It will therefore be of importance only for me to describe the alteration which I make when I employ it for the purpose of detecting arsenic. In the first place, I must observe that the outer vessel (*a*) which I use holds full four pints, and that the jet of the stopcock is vertical, and its orifice is twice or three times larger than in the instrument as generally

made for sale, and also that there is a thread or wire attached to the cork of the stopcock (*b*) for suspending a piece of zinc (*c*) within the bell glass.

"With an instrument of this description I have operated on 1 grain of arsenic in 28,000 grains of water (or four imperial pints), and have obtained therefrom upwards of 100 distinct metallic arsenical crusts. Similar results have been obtained with perfect success from three pints of very thick soup, the same quantity of port wine, porter, gruel, tea, coffee, &c. &c.

"It must be understood that the process was slow and required several days before the mixture used ceased to give indication of the presence of arsenic, and also a much larger portion of zinc and sulphuric acid was employed from time to time than when working with the small bent tube apparatus, in consequence of the large quantity of matter operated on under this arrangement.

"With the small apparatus I have obtained distinct metallic crusts when operating on so small a quantity as one drop of Fowler's solution of arsenic, which only contains $\frac{1}{120}$th part of a grain. The presence of arsenic in artificial orpiment, and realgar, in Scheele's Green and in the sulphuret of antimony, may be readily shown by this process when not more than half a grain of any of those compounds is employed. In conclusion, I beg to remark that although the instruments I have now finished describing are the form I prefer to all I have employed, it must be

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perfectly evident to any one that many very simple arrangements might be contrived. Indeed I may say unequivocally there is no town or village in which sulphuric acid and zinc can be obtained but every house could furnish to the ingenious experimentalist ample means for the purpose. For a two-ounce phial, with a cork and a piece of tobacco-pipe, or a bladder with the same arrangement fixed to its mouth might, in cases of extreme necessity, be employed with success, as I have repeatedly done in this instance. The only ambiguity that can possibly arise in the mode of operating above described, arises from the circumstance that some samples of zinc of commerce themselves contain arsenic; and such when acted on by dilute sulphuric acid gave out arseniuretted hydrogen. It is therefore necessary for the operator to be certain of the purity of the zinc which he employs, and this is easily done by putting a bit of it into the apparatus with only some dilute sulphuric acid, the gas thus obtained to be set fire to as it issues from the jet, and if no metallic film is deposited on the bit of flat glass, and no white sublimate within the open tube, the zinc may be regarded as in a fit state for use."

Doubtless some of the readers of this book will be surprised to find that Marsh's process, when it left the hands of the master, was capable of dealing with *mixtures* of arsenious acid with the various common articles of food and drink without demanding, as a

preliminary operation, the destruction of the organic matter. And the author of this book expects that most chemists will be surprised to learn that Marsh himself claimed for his method that it "eliminates the whole of the arsenic in the state of arseniuretted hydrogen." In order that the elimination may be complete, it is essential to conduct the operation in a proper manner; and a careful and intelligent study of the text of Marsh's paper (which has just been quoted without alteration) will enable the reader to verify the justice of the claims which have been brought forward. It will be noted that one of the conditions of success is that the development of hydrogen must be very gradual and protracted.

In France and Germany Marsh's test has been well appreciated and likewise developed in a remarkable manner. When the stream of hydrogen (laden as it is with arseniuretted hydrogen) issues from the Marsh apparatus, there are other ways of utilising it besides burning it or passing it through a red-hot tube. The gas may be passed into various solutions containing salts of the various heavy metals, and most interesting and important are the chemical events which come to pass.

Thus, when in the year 1874 in France, Mayençon and Bergeret passed the stream of gas, as it issued from the Marsh apparatus, into a solution of corrosive sublimate, they reported that the following change took place:—

$$6HgCl_2 + 2AsH_3 = 3Hg_2Cl_2 + As_2 + 6HCl.$$

Solution of perchloride of mercury (corrosive sublimate) and arseniuretted hydrogen are resolved into subchloride of mercury (calomel) and metallic arsenic and hydrochloric acid. The action is prompt, and is available for rendering quantitative results.

The mixed calomel and metallic arsenic form a precipitate, which by filtration may be collected upon filter paper, and subsequently weighed and investigated in many ways which would suggest themselves to a chemist.

From an analytical point of view this manner of dealing with arseniuretted hydrogen offers a very striking advantage. Make the calculation by replacing the chemical symbols in the equation by the proper numbers, and it will be found that 150 parts of metallic arsenic received in the state of arseniuretted hydrogen by the solution of corrosive sublimate yields 1563 parts of mixed calomel and metallic arsenic.

If arsenic were estimated in that way, one unit of arsenic would be represented by 10.42 of the solid to be weighed.

An investigation made in the author's laboratory has confirmed the substantial accuracy of the report. The unit of arsenic in the shape of arsenious acid is represented by rather more than 10.42 units of the dry precipitate. The author is of opinion that the metallic arsenic is not in mixture with the calomel, but in real chemical combination.

The two French chemists above mentioned have

employed this method as a means of distinguishing between the antimony and the arsenic compounds with hydrogen, both of which are gases.

With that object in view they place a little of the solution of corrosive sublimate on glazed white paper, and hold the paper in the stream of gas. If arseniuretted hydrogen be there, a citron-yellow stain makes its appearance, and after a while the stain assumes a brown-yellow colour. Antimoniuretted hydrogen, on the other hand, strikes a dark grey colour which cannot be mistaken for the arsenical spot. Experiments on the delicacy of the method have been published showing that solutions with one part of arsenious acid in 70,000 parts of the solution strikes the citron-yellow colour in one minute, and that solutions with one part in 120,000 require five minutes in order to produce the stain.

Arseniuretted hydrogen and solution of nitrate of silver react as follows:—

$$6AgNO_3 + AsH_3 + 3H_2O = 6HNO_3 + Ag_6 + AsO_3H_3.$$

The AsO_3H_3 is, of course, resolved into water and arsenious acid, thus:—

$$2(AsO_3H_3) = As_2O_3 + 3H_2O.$$

When the gas issuing from Marsh's apparatus is passed into the solution of nitrate of silver, the first visible effect is that the silver-solution darkens, assuming a brownish-black colour; then, as the passage of

the gas is continued, a voluminous black precipitate separates from the liquid which gradually settles down and contracts and consists of metallic silver. The solution gradually becomes acid, and is found to contain arsenious acid, the presence of which may be manifested by adding with great caution, drop by drop, dilute solution of ammonia, so as to neutralise the liquid, whereupon the yellow arsenite of silver will make its appearance.

The behaviour of the gas towards silver-solution affords a means of distinguishing between the gaseous compounds of arsenic and antimony. Arseniuretted hydrogen throws down pure silver, and charges the solution with arsenious acid: antimoniuretted hydrogen throws down an alloy of antimony and silver, and no antimonial compound enters into the solution.

The author of this book has carried out experiments with the object of ascertaining the practicability or otherwise of making estimations of arsenic by the employment of this reaction in order to deal with the stream of gas from Marsh's apparatus. On inspection of the equation given above it is manifest that every atom of arsenic passed into the nitrate of silver should reduce six atoms of silver; therefore, every unit of arsenic is represented by 9.12 units of metallic silver. As a product of the reaction there is the arsenious acid in the solution, and that may be converted into sulphuret of arsenic and weighed in that form, or else it might be oxidised into arsenic acid and weighed as

arseniate of magnesia. The author has weighed the precipitated silver, filtering off the solution containing the As_2O_3, oxidised and finally weighed the arsenic acid as salt of magnesia.

Many difficulties of detail stood in the way, but they have been so far overcome that the author has no hesitation in making the announcement that the Marsh test, worked by passing the gas through solution of nitrate of silver, affords a useful quantitative determination of the arsenic.

The initial difficulty was, of course, how to prevent the greater part of the arsenic from becoming masked by passing into states of existence other than the state of the gaseous compound of arsenic and hydrogen. One of the devices resorted to in order to avoid that calamity was to keep the acid in the Marsh apparatus in slight excess over the zinc. Strict account is kept of the quantities of zinc and acid employed; and the form of the apparatus has been somewhat altered in order to facilitate the different steps which have to be taken.

Another point requiring attention was how to insure complete action between the gaseous arsenic compound and the silver-solution. The gas proceeding from a Marsh's apparatus is, of course, dilute arseniuretted hydrogen—*very dilute indeed* in most cases. Unless proper precautions be taken the vast volume of free hydrogen will protect the arseniuretted hydrogen from the silver-solution, and in that way the determination of arsenic would be damaged.

The strength of the silver-solution has also received attention, and a one per cent. solution, *i.e.* one gramme of nitrate of silver in 100. c. c. of distilled water, has been found to answer.

The internal capacity of the gas-generating vessel employed in these experiments was 270 c. c.: the generator being a very strong glass bottle with a strong neck into which fitted a good cork properly bored. The granulated zinc employed was carefully weighed and gradually introduced; and some idea of the ratio of hydrogen to arsenic volatilised may be gathered from the statement that 14.56 grammes of zinc were dissolved in the generating vessel and 0.494 gramme of reduced silver was weighed. After that had taken place a further introduction of 2.34 grammes of zinc with the necessary acid occasioned no further ponderable reduction of silver.

The study of the chemical action which takes place in Marsh's apparatus leads to the conclusion that the reduction of As_2O_3 so as to yield up the arsenic in the form of $2AsH_3$ proceeds by stages.

The equation

$$As_2O_3 + 6H_2 = 2(AsH_3) + 3H_2O$$

expresses the final effect; but there are evidently stages in the operation carried on in the gas-generating vessel. A first portion of the gas comes over with great facility, and direct experiment has proved that much, if not absolutely all of the masked arsenic, *remains in the clear solution.*

There is no difficulty in converting half of the arsenic existing in arsenious acid into arseniuretted hydrogen, but to obtain nearly the whole in the form of arseniuretted hydrogen (though quite possible) is rather tedious.

The author offers the following suggestion. First stage of the reaction :—

$$As_2O_3 + 4H_2 = AsH_3 + AsH_2O_2H + H_2O.$$

The hypothetical body AsH_2O_2H, would be the hydrogen representative of kakodylic acid, slowly attacked by long-continued hydrogenation in the Marsh's apparatus. Whether this hypothesis be the true theory of the changes or not, the fact is established that whether the scale be great or small there is a first outburst of arseniuretted hydrogen until about half of the possible arseniuretted hydrogen has been given off, and then the yield slows down and ultimately stops.

The theory derives some support from an experiment in which to begin with the arsenic must have been in the state of arsenic acid, and when for a while there was almost absolutely no evolution of arseniuretted hydrogen and then a slow evolution of the arsenical gas.

The author is studying the action of different solutions on the gas from the Marsh apparatus. So far as his experiments have gone, he prefers the solution of corrosive sublimate.

Section 2.—Reinsch's Test.

Edgar Hugo Emil Reinsch, born in the year 1809, was the discoverer of the well-known Reinsch's test, apparently about the year 1842. He died in Erlangen, 1st November 1884.

In Fownes's "Manual of Elementary Chemistry," published in the year 1844, there is the following passage on page 316:—

"A slip of copper-foil boiled in the poisoned liquid, previously acidulated with hydrochloric acid, withdraws the arsenic and becomes covered with a white alloy. By heating the metal in a glass tube the arsenic is expelled."

At that date Fownes was Chemical Lecturer in the Middlesex Hospital Medical School and to the Pharmaceutical Society of Great Britain, and his excellent and most interesting manual was, no doubt, the means of introducing this test to Englishmen. By an oversight, no doubt, purely accidental, the name of Reinsch was not mentioned by Fownes, the passage above quoted being the concluding paragraph of the section on arsenic, and immediately following the detailed account of the Marsh's test, which was duly ascribed to *Mr. Marsh.*

The seeming simplicity of this test at once commended it to attention in England, and Taylor of Guy's Hospital made abundant use of it in medico-legal inquiries.

The principle of the test is quite intelligible. Arsenious acid As_2O_3, hydrochloric acid HCl, in somewhat dilute aqueous solution, and metallic copper Cu_2, finding themselves together, react thus :—

$$3Cu_2 + As_2O_3 + 6HCl = 3H_2O + 6CuCl + As_2.$$

The 6CuCl dissolves in the hydrochloric acid and the As_2 combines with the surface of the copper-foil, producing the white-grey alloy of copper and arsenic, and clings to the copper. On heating the coated copper-foil to low redness the alloy is decomposed and the arsenic sublimes and oxidises, and may be collected on the inside surface of a narrow glass tube in the form of glittering crystal of As_2O_3. The copper-foil acts as a sort of sponge for the collection of the arsenic which exists in the liquid submitted to the operation of the Reinsch's test.

It is quite true that for every equivalent of oxygen in the arsenious acid an equivalent of copper passes into solution, and to that extent the copper-foil is used up, but for the rest the action of the copper is that of a carrier, an arsenic-carrier.

In the year 1861, a distinguished German chemist of the name of Werther published an important observation which he had made in working Reinsch's test. He found that solutions containing even a considerable proportion of arsenic acid, or of salts of arsenic acid, dissolved in hydrochloric or sulphuric acid did not at all readily cause the well-known arsenical coating of the

slip of copper-foil. Months of contact in the cold produced no arsenical coating; alternate boiling and cooling of the solutions with the slip of copper-foil immersed in them were equally without effect. And the conclusion arrived at by Werther was that only arsenious acid and its salts (and not arsenic acid and its salts) is capable of giving the arsenical coating to a slip of bright copper-foil by short immersion in the boiling acid liquid.

Many quantitative experiments were recorded in which time and proportions of arsenic were noted, and the general result was that as much as *one per cent.* of arsenic (700 grains per gallon) in the shape of arsenic acid was needed in order that the slip of copper might acquire an unmistakable arsenical coating by short boiling in the acid liquid.

Werther showed also that a solution of *cupric* chloride in hydrochloric acid dissolved metallic arsenic when the solution was gently warmed.

Reinsch himself has verified and confirmed much of Werther's work.

Reinsch admits that when the dilute solution of *arsenic acid* is mixed with half its volume, or even its own volume of strong hydrochloric acid, the Reinsch test utterly fails to detect traces of arsenic.

But Reinsch insists upon the validity of his test when the proportion of hydrochloric acid is so much increased that there are two volumes of strong hydrochloric acid to one volume of the arsenical solution.

"The acid solution must be so strong that the copper is attacked, otherwise the arsenic acid is not reduced." Reinsch maintains that with a sufficiency of hydrochloric acid, *i.e.* two volumes of the strong acid to one volume of the dilute solution of arsenic acid, the production of the arsenical coating is almost instantaneous, and that one part of arsenic is distinctly to be recognised in 100,000 parts of the arsenical solution, just as if it were present in the state of arsenious acid. In the same year, viz. 1861, E. C. Stanford, in this country, called attention to the fact that the presence of so common a substance as perchloride of iron in the supposed arsenical solution would bring about discoloration of the slip of copper in the Reinsch's test. Attention was likewise directed to the fact that most, if not all, commercial copper is more or less arsenical, and in 1863 a very curious paper was brought before the Chemical Society of London by Dr. William Odling, F.R.S. The paper bore the title "Note on the Detection of Arsenic in Copper," and opened as follows:—

"As even in the most satisfactory performance of Reinsch's test for arsenic—the deservedly favourite test of English toxicologists—there is always some, although but an extremely small quantity of the copper wire, foil, or gauze dissolved, and as commercial copper is rarely quite free from arsenic, and sometimes contains a very notable proportion thereof, it is important that the copper to be used in medico-

legal researches as a precipitant for arsenic should be specially tested as to its purity."

After some further remarks Dr. Odling proceeds:—

"A few grains of the copper cut into small pieces are placed in a small tube-retort with an excess of hydrochloric acid and so much ferric hydrate or chloride as contains a quantity of iron about double the weight of the copper to be acted upon. The mixture is then distilled to dryness, some care being taken at the last to prevent spurting. The whole of the copper is in this way quickly dissolved, and any arsenic originally contained in it carried over in the form of chloride of arsenic, which may be condensed in a little water with the excess of aqueous hydrochloric acid. The resulting distillate is then tested for arsenic."

In the next year, viz. 1864, Hellwig published in Germany an account of the employment of the microscope in toxicology, in which he described a mode of procedure by which very minute quantities of arsenic, deposited on glass or porcelain, might be sublimed and in that way transferred to the slide of the microscope, where the characteristic form of the crystals of arsenious acid might be verified. Of course this method is of general application whether the trace of arsenical deposit were derived from the deposit by Marsh's test or Reinsch's test, or deposit produced in other ways. Hellwig especially noted that, whereas an arsenical deposit would yield a sublimate

of As_2O_3 crystals, a deposit of pure antimony gave nothing.

In comparing Marsh's and Reinsch's tests, the first point is that neither the one nor the other is capable of dealing with the case where the arsenic has entered into the organo-metallic state. Applied to kakodylic acid, for instance, both would fail.

But *arsenious acid* in mere mixture with organic matter is to be recognised easily by either Marsh or Reinsch.

Arsenic acid, under like conditions, is to be recognised by Marsh's test, but not by Reinsch's test, as it has been recently described in a very modern document, to which reference will presently be made. By Reinsch's test, *when abundance of hydrochloric acid is used,* as Reinsch himself recommended in the year 1861, arsenic acid may be recognised. The seeming simplicity of the Reinsch test is more apparent than real. The necessity of having the copper free from arsenic is a source of trouble to the operator; and the advice may be given that before resorting to the Reinsch test a preliminary experiment should be made in order to see whether or not the copper-foil itself is capable of throwing off arsenic and causing a sublimate of arsenious-acid crystals on the microscope-slide.

The hopelessness of the Reinsch test, from a quantitative point of view, is in great part due to the circumstance that there can be no action of the test

without some of the copper passing into solution; and the entrance of copper into solution arrests the deposit of arsenic on the copper, and even, under some conditions, brings about re-solution of arsenic already deposited. Werther's important investigation, an abstract of which will be found in the *Jahresbericht* for the year 1861, to which reference has been made, is very much to the point. The absolute absence of any relation between the amount of discoloration of the copper-foil and the quantity of arsenic in the liquid is fatal. The employment of one very obvious way of attempting a rough quantitative employment of the test, coupled with the resort to the microscope for the appreciation of the crystals of As_2O_3, brings in its own peculiar difficulties and uncertainties.

The following recent experiment performed in the laboratory of the author may be cited. A mixture of 200 c. c. of London water from the Lambeth Water Company, 15 c. c. of a solution containing one milligramme of As_2O_3 per cubic centimetre of the solution, and 30 c. c. strong hydrochloric acid was subjected to the Reinsch's operation in the manner approved by the brewers' experts to which reference will presently be made. First one lot of copper was introduced, and in due time, after the prescribed boiling in contact with the solution, it was taken out, washed, dried, and heated, and abundant As_2O_3 sublimed. Then a second lot of copper was put into the solution and treated as before, and As_2O_3 obtained. And finally the residual

solution was placed in the Marsh apparatus, and still it evolved abundance of arsenic.

Since the year 1864 some branches of chemical analysis have decayed in England. The following passage, quoted from the report of the commission of experts appointed by the Manchester Brewers' Central Association to investigate the circumstances of the arsenical beer poisoning, affords a curious example of such decay:—

"The most important matter for the moment is to secure adequate testing of beer in order that the public may be protected from further mishap. Arsenic is a substance which can be detected in the most infinitesimal quantities by those who are practised in the tests, but these tests are so delicate that they are apt to mislead those who have not had experience in their application, and this is more particularly the case when the test is to be applied to a complex mixture such as beer. Accordingly, the commission have thought it necessary to investigate and determine what is the most suitable method of testing beers for arsenic.

"*Test.*—The commission recommend that the Reinsch test should be used in preference to all others at present known, because their investigations have satisfied them that it is the best and most reliable test for arsenic in beer. The mode of performing it is as follows: Take 200 c. c. of the beer in a porcelain evaporating-dish. Raise the liquid to the boiling-point,

and then add 30 c. c. of pure concentrated hydrochloric acid. Insert a piece of pure bright copper-foil about a quarter of an inch by half-an-inch in size, and keep the solution gently boiling for forty-five minutes. If at the end of that time the copper remains bright and red, the beer is free from arsenic.

"If a deposit is obtained on the copper, the foil is to be washed successively with water, alcohol, and ether (care being taken that these are pure), dried at a temperature not exceeding 100° C., and subjected to slow sublimation in a thin reduction-tube of small section, and not less than two inches long, the upper portion of which should be warmed before the sublimation begins. For the purpose of the sublimation a small spirit-lamp flame should be used. If any sublimate be obtained, it must be examined under a magnifying power of 200 diameters. Any sublimate which does not show well-defined octahedral or tetrahedral crystals is not to be considered arsenical.

"*N.B.*—It must be borne in mind that the blackening of the copper or a deposit thereon from the preliminary operation does not demonstrate the presence of arsenic in beer. Abundant blackening and deposit may be obtained from the purest beer."

Reading this report a chemist might be tempted to imagine that the real object of the commission of experts was to burke inquiry and to prevent the finding of any arsenic that the beer might have contained. Restrict yourself to Reinsch's test, and

(notwithstanding that Reinsch, when he was alive, warned chemists that the arsenic existing in the form of arsenic acid required 400 c. c. of strong hydrochloric acid) take only 30 c. c. of acid with the 200 c. c. of beer—that was the recommendation of this commission in the year 1900.

Among chemists, certainly among chemists as they were thirty or forty years ago, it was customary to control and verify chemical analysis, by resorting to more than one method if that were practicable; but these experts of the Manchester Brewers' Central Association set their faces against anything of that kind in this instance. They "recommend that the Reinsch test should be used in preference to all others at present known." In 1844 Fownes placed Marsh's test first, and the copper process of Reinsch in a quite subordinate place. In 1900 a commission of experts restricts itself to the Reinsch test. Verily, in official England that part of chemical analysis which is concerned with arsenic has undergone a process of degeneration since Fownes wrote his manual in the year 1844.

One of the curious features of this report—and that feature has attracted public attention in various quarters—is the complete absence of any quantitative result. The experts reiterate the statement that the sulphuric acid used by Bostock & Company of Liverpool was arsenical, and that Bostock's sugar became arsenical, and that beer brewed from Bostock's sugar

was arsenical, but they do not disclose the degree of the arsenical contamination. Why is that? There is one answer (and it would be a perfectly honest answer, and as appears to the author of this book, it is the only possible honest answer under all the circumstances). That answer is that they themselves had followed the advice given in their report. Their chemical examination was restricted to the use of Reinsch's test, and Reinsch's test is not quantitative, and, therefore, they had no quantitative results. They did not know the degree of the arsenical contamination either of acid or sugar or beer.

In the opinion of the author of this book such an investigation as would have given quantitative results was possible if the experts had availed themselves of the resources of analytical chemistry as understood in France and Germany.

Section 3.—General Testing and Estimation of Arsenic.

The almost universal diffusion of arsenic to which attention was called in Chapter I., page 15, constitutes one of the chief difficulties with which the chemist has to contend in all cases of the analysis of materials which contain or are suspected of containing arsenic; and the necessity of making sure that nothing employed in the analysis contains arsenic must be obvious. All the reagents should be specially tested for arsenic, and for that purpose the Marsh's apparatus is most useful.

In carrying out these testings it is to be recommended that *method* be insisted upon; and that a quantitative character should be given to the results. Thus, for instance, in testing the hydrochloric acid a given volume of acid should be taken, say 50 c. c., and a given quantity of zinc dissolved in the Marsh's apparatus, and the result recorded that *there is*, or that *there is not*, the first indication of a trace of arsenic.

One of the reagents used in estimating arsenic is sulphuretted hydrogen, and in Watts's Dictionary of Chemistry, vol. i. page 367, the following passage occurs: "Sulphuretted hydrogen, evolved by the action of dilute sulphuric acid on sulphide of iron, often contains arsenic proceeding from one or both of the substances used."

In order to make sure of the purity of the sulphuretted hydrogen the following procedure might be resorted to:—

A given weight of the sulphuret of iron being placed in the generating apparatus, a measured volume of diluted hydrochloric acid or diluted sulphuric acid should be gradually poured into the apparatus, and the sulphuretted hydrogen passed into a small Woulff's bottle containing excess of solution of caustic potash or soda, which would absorb the sulphuretted hydrogen but not the free hydrogen gas, which generally accompanies it, and not the arseniuretted hydrogen if any should be present. The Woulff's bottle should

be provided with two necks, through one of which the tube conveying the sulphuretted hydrogen enters, and the other should give exit to another tube to convey any unabsorbed gas and deliver it into another vessel charged with a solution of nitrate of silver. In that way any arsenic existing in the sulphuretted hydrogen would be sure of detection.

When the passage of the sulphuretted hydrogen is complete, the vessel containing the silver-solution might be detached and dilute ammonia very carefully added to the silver-solution (previously filtered if necessary), in order to show the presence or absence of yellow arsenite of silver. Finally the potash solution which has absorbed the sulphuretted hydrogen might be supersaturated with hydrochloric acid, in order to disclose the presence of the yellow sulphuret of arsenic, if by any chance any arsenic had been absorbed.

Sulphuretted hydrogen is so important a reagent in the general scheme of the analysis of substances containing metals that chemists require a ready way of preparing it in a condition in which its purity from arsenic is above suspicion. Obviously the solution of sulphuretted hydrogen in caustic potash or soda supplies this want. This solution being placed in an ordinary gas-generating bottle, requires only to be cautiously treated with hydrochloric acid in order to evolve sulphuretted hydrogen gas free from arsenic, inasmuch as any arsenic would remain behind in the state of sulphuret in the gas-generating vessel.

One of the best methods of measuring the amount of arsenic, or estimating as it is termed, is by converting the arsenic into the sulphuret of arsenic and weighing the sulphuret. The percentage composition of sulphuret of arsenic As_2S_3 is as follows:—

As_2 . .	150	69.72
S_3 . .	96	30.28
	246	100.00

The factor to multiply by, in order to calculate the amount of arsenic from the weight of the sulphuret, is therefore 0.6972.

In the recent epidemic of suspected arsenical poisoning in the North of England, where the root of the mischief is said to have been the arsenical sulphuric acid employed in the transformation of starch into sugar, one of the best methods of analysing the sulphuric acid would have been by the conversion of the arsenic into sulphuret of arsenic, and the weighing of that sulphuret. According to one of the reports which has found its way into the public press, some of that sulphuric acid contained as much as about 2 per cent. of arsenic. A convenient quantity of such acid would be about 10 grammes. If we suppose that quantity to have been weighed out, the steps of the analysis would be as follows: First it would be well to dilute the acid with 50 c. c. of distilled water, and if necessary to filter through a small filter, carefully washing the filter. The filtrate would then receive a little

sulphurous acid, which might be made by heating sulphuric acid and wood charcoal in a very small flask-retort provided with a gas-delivery tube. The gaseous sulphurous acid would be passed into the liquid to be analysed, until there was a strong smell of sulphurous acid; then the evolution of SO_2 would be stopped and the liquid would be heated to boiling, and so the arsenic, if originally existing as arsenic acid, would be brought into the condition of arsenious acid, and the excess of unacted upon sulphurous acid would be driven off. The next step would be passage of sulphuretted hydrogen into the liquid, and the leaving for a while of the liquid charged with the H_2S, and corked up so as to exclude the atmosphere as much as possible. In that manner the arsenic originally in the sulphuric acid is made to yield the bright yellow sulphuret of arsenic, which would next be separated from the liquid by filtration, and washed with cold water. Probably the sulphuret of arsenic would be mixed with more or less sulphuret of lead, and the colour of the precipitate would be dark and brownish owing to the presence of the lead. A separation of the sulphuret of arsenic from the sulphuret of lead is easily effected by means of a solution of carbonate of ammonia, which dissolves the As_2S_3 and leaves the sulphuret of lead and other sulphurets as an insoluble black powder. The solution in the carbonate of ammonia may be decomposed with dilute hydrochloric acid and the As_2S_3 reprecipitated, filtered, washed, dried,

and weighed. Assuming the correctness of the report that there was 2 per cent. of arsenic in the original acid, the weight of the sulphuret of arsenic from the ten grammes of acid would be 0.2869 gramme.

The sulphuret of arsenic might be mixed with charcoal and carbonate of soda, and the mixture heated to redness in a tube of hard glass, and in that manner made to give a mirror of metallic arsenic; but some of the arsenic obstinately refuses to become reduced under these circumstances.

Another way of dealing with the sulphuret is to oxidise it with nitric acid or aqua regia, and convert it into arsenic acid and sulphuric acid, and then to make the ammonio-arseniate of magnesia, which, on gentle ignition in a porcelain crucible, becomes pyro-arseniate of magnesia, which may be weighed. The composition of the pyro-arseniate of magnesia is:—

As_2	150	48.39
Mg_2	48	15.48
O_7	112	36.13
	310	100.00

and the factor for the calculation of the amount of arsenic from the weight of the pyro-arseniate of magnesia is 0.4839.

The other forms in which arsenic may be advantageously weighed are the metallic state and in the form of arsenious acid.

In the absence of sulphur, an arsenite or an arseniate

of potash or soda is totally reduced to the metallic state when it is mixed with a sufficiency of charcoal and heated to redness, and if the operation be performed in a narrow tube of hard glass closed at one end, and several inches in length and open at the other end, the metallic arsenic will form a mirror on the inside of the tube. After the tube has cooled, and with the metallic arsenic adherent to the inside, it may be weighed, and then the arsenic may be volatilised and the empty tube again weighed. The difference between the two weighings is the weight of the metallic arsenic. When sulphur is present, difficulties arise owing to the formation of sulphur salts—arseniates wherein the oxygen has been replaced by sulphur —which possess very great stability. Under these conditions there is very great difficulty in effecting a complete volatilisation of every trace of arsenic. The remedy is to take care that there is a considerable excess of alkali or alkaline carbonate, and to pass a slow current of air over the red-hot mass.

Incidentally the remark, that commercial copper contained more or less arsenic, was quoted on page 61. The reader will be prepared to learn that traces of arsenic, and often more than traces of arsenic, are most obstinately retained by some of the heavy metals.

Trustworthy analyses are on record of some of the best English copper, showing as much as ten grains of arsenic in the pound of copper: and Mexican copper

has been known to contain two or three per cent. of arsenic.

When lead is heated with arsenic it forms a brittle alloy, greyish-white in colour, and very fusible. On being strongly heated much of the arsenic is driven off, but a certain proportion of arsenic remains behind with the lead, and is not capable of being driven off. Shot consists of an alloy of lead and arsenic, which contains 1.7 per cent. of arsenic.

The correct measurement of these minute proportions of arsenic in masses of the heavy metals is often a very difficult task, demanding great skill on the part of the analyst.

Section 4.—Special Organo-Metallic Condition of Arsenic, &c.

Passing on to that which more particularly falls within the scope of this book, viz. the poisoning of articles of food or beverages by arsenic, the relations of the arsenic to organic contents will next be considered.

When arsenic is put into an organic mixture either of two things is possible. The arsenious acid may remain in the mixture in the form of arsenious acid, or its salts, or it may enter into intimate relations with the organic matter as it is peculiarly prone to do. If it remains in the state of arsenious acid, or its salts, it will be recognisable by the ordinary tests, but if it should enter into the peculiarly intimate relation

known as the organo-metallic state, then the ordinary tests fail except such as involve destruction of organo-metallic compounds.

The application of a red heat breaks up organo-metallic combinations, and in all cases where the formation of organo-metallic combinations is suspected the testing for arsenic should be so carried out as to involve such an operation as a preliminary. Neither the usual destructive action of chlorine on the organic matter, nor of a mixture of chlorate of potash and hydrochloric acid, nor of sulphuric acid, quite takes the place of an operation in a combustion-tube, such as is now recommended.

The chemical history of kakodylic acid, which is a representative of possible organo-metallic arsenical compounds, conveys a warning against trusting any oxidising agent at ordinary temperatures, and nothing short of a furnace operation in the combustion-tube will be satisfactory.

Failing such an investigation of the sugar and beer which is credited with causing the Manchester epidemic, that epidemic will remain an unsolved mystery.

The mode of operation to be followed in the instance of suspected arsenic organo-metallic products will now be sketched out.

The suspected beer may be examined in this manner, the following being the working directions.

Take 100 c. c. of the beer, add one gramme of pure quicklime slaked with a little water, and evaporate

down in a clean porcelain dish in the water-bath. When three-quarters of the liquid have evaporated add 10 grammes of recently ignited sand, and continue the evaporation down to dryness in the water-bath. The residue (which is a mixture of the dry residue of the beer with the sand and lime) is to be placed in a combustion-tube, such as is employed in the well-known elementary organic analysis.

The combustion-tube is drawn out to a point at one end in the well-known manner, and the point is closed by fusing the glass. The charge placed in the tube is, first, 3 inches of very coarse sand at the closed end; second, about 9 inches of the mixed lime, sand, and beer residue, and then 3 inches of very coarse sand and an asbestos plug. Then an inch or so in front of the asbestos plug (after the tube has been charged as described) the tube is to be contracted and drawn out by the aid of the table-blowpipe, and finally so drawn out as to terminate in front in a gas-delivery tube which may be bent and made to deliver gas under water. The arrangement will be perfectly understood by any chemist who has performed a combustion of an organic substance containing mercury.

The combustion-tube, charged as described, is then placed in the well-known furnace in which organic analyses are carried out, and heated thus:—

The heat is applied to the tube so that the asbestos plug and three inches of sand in the front part of the tube are heated to redness, and the closed end of the

tube is also heated, and then very gradually the mixture of beer residue, &c., is made red hot, the heating being from before backwards in the slow and deliberate manner which chemists who have made organic analyses will understand. By degrees the beer residue will be converted into a carbonaceous mass mixed with sand and a little lime, and into gases and vapour, for the most part aqueous, which will condense in the front part of the tube, carrying with it any arsenic that may have been contained by the beer. The gas-delivery tube, in which the front of the combustion-tube terminates, should pass into a small quantity of water contained in a very small beaker.

The combustion-tube, as was explained, is of the usual kind, the hinder part terminating in the usual narrow *tail*. The proper ending of the operation consists in breaking off the extreme tip of this tail and affixing a narrow india-rubber connecting-tube conveying a slow stream of air or oxygen from a small gas-holder, in order to burn up some of the carbonaceous deposit and sweep all traces of arsenic into the small quantity of water, or into the extreme front of the combustion-tube. The small volume of water in the beaker which receives the volatile products of the operation may be treated in many ways. It may be charged with a little chlorine water, so as to convert any traces of arsenic into arsenic acid; and the ultimate destiny of the product may be the Marsh's apparatus, depending upon the judgment of the chemist.

Of course a most careful scrutiny of the front part of the tube should be made at the end of the operation, and when the tube has cooled down to ordinary temperatures. If any sign of deposit be present it will be necessary to cut the narrow part with a file, and to wash out the front extremity with an appropriate solvent for traces of arsenic.

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CHAPTER III.

THE MANCHESTER EPIDEMIC OF ARSENICAL POISONING AND THE LESSONS TO BE LEARNT FROM IT.

MANCHESTER, which at the last census had a population of 505,368, and Salford with its population of 198,139, form, in point of fact, one large township; the one occupying the one bank of the narrow river Irwell, and the other occupying the opposite bank of the river. The Manchester epidemic about to be described was shared by Salford, and the conjoint population, which at the last census was about 700,000, will no doubt be found to be rather more than that figure when the new census is taken a few weeks hence.

The following extract from the *Manchester Guardian* of the 23rd November 1900, followed by the reports of the medical officers of Salford and Manchester, will convey an idea of the epidemic:—

"An extraordinary state of affairs has just been revealed at some of the hospitals in Manchester and the district. At present the circumstances would appear to point to a general epidemic of arsenical poisoning, caused, it is believed, by the consumption

of impure beer. The matter is under investigation by medical men who are interested in the cases. The hospital connected with the Manchester Union Workhouse at Crumpsall seems to have received a large number of cases. Three months ago the Master (Major Ballantine) noticed that the lists of patients from outside the workhouse who had been admitted to the hospital showed a striking inflation when compared with those for the corresponding period of previous years. The patients continued to increase with such rapidity, in fact, that soon there were some 250 more inmates of the hospital than there had been twelve months before. The attention of Dr. Reynolds, the resident medical officer at the workhouse, was drawn to the matter, and that officer commenced a thorough examination of the people under his charge. It seems that Dr. Reynolds had noticed for some time previously that a large percentage of his patients were apparently suffering from the effects of drink. He now discovered that the common complaint was aggravated in a greater or less degree by arsenical poisoning. Continuing his investigations, he ascertained that beer obtained from the same sources as that consumed by the invalids contained traces of arsenic. Dr. Reynolds, along with Dr. Niven (officer of health for Manchester) and other medical men, have, we understand, made a thorough inquiry into the matter, and a report dealing with the whole subject is about to be published. So far as can be

ascertained, no deaths have occurred which can be directly attributed to the drinking of the beer. The case of the Crumpsall Workhouse, however, is not by any means an isolated one, for the 'complaint,' if it may be so described, is almost equally prevalent in Salford as in Manchester. It is interesting to note that in his weekly return of the health statistics of the city, Dr. Niven, the medical officer of health, states that on the last day of the week ended November 17, 1900, there remained in the Manchester Union Infirmary 1099 sick paupers, as compared with 885 at the end of the corresponding week of last year."

At a special meeting of the Salford Health Committee, held on 26th November 1900, the following report was submitted by the medical officer:—

"I regret to have to report that there has been a very serious amount of sickness, which is apparently due to arsenical poisoning, in the borough during the past four months. In the third week in July there were three deaths registered in the borough as due to 'peripheral neuritis,' 'multiple neuritis,' or 'alcoholic neuritis.' This was followed week by week by the following numbers up to the present date, viz.: 0, 1, 1, 1, 2, 2, 1, 2, 4, 2, 1, 2, 3, 3, 4, 5, 2, and 2, or a total of 41. In addition to these deaths there have been 25 certified to be due to alcoholism in the same period. To realise exactly the bearing of these figures it should be stated that in the first seven months of

the year there were 22 deaths, as compared with 66 in the past four months. In the year 1899 there were 19 deaths from multiple neuritis, and 20 from alcoholism. In 1898 the figures were 14 and 17 respectively, and in 1897 10 and 17. My attention was naturally called to these figures, but as 20 out of the total cases gave other causes of death, such as pneumonia, phthisis, thrombosis, influenza, bronchitis, &c., it appeared probable that the cause for the increase was more in the method of certifying than any marked change in the causes of death. Casual inquiries among a few friends confirmed this view, as they had no special amount of sickness of this character in their practices. It must not be forgotten that the whole of these deaths cannot be attributed to the poisoning, for on the average of the deaths from similar causes in the preceding three years there would have been 15 deaths in the period under notice, without any disturbing influence, so that this leaves a balance of 51 deaths due to the special disease under notice. I have no means of ascertaining the number of cases of sickness, but from the inquiries made it is evidently very great. There have been 100 cases treated by the district Poor-law medical officers, out of which eight have died.

"On the 9th of November, Dr. Cran, the Poor-law medical officer for the Regent district, called on me to draw my attention to the large amount of illness of a paralytic nature in his practice, which he had

concluded was due to beer-drinking. On that day five samples of beer were obtained and sent to the public analyst, and a further ten samples in the few days following. He, however, failed to find anything to account for the illness. Having ascertained that there was a very great number of cases of illness in the borough of this character, I saw Professor Delépine, of the Owens College, and arranged for him to make certain experiments with a view of ascertaining the cause of the prevailing sickness. In the meantime inquiries were made into the details of all the cases that could be heard of, and it became abundantly evident that the one thing common to them all was beer-drinking, not necessarily to excess, as many of the cases were only those of moderate drinkers; and it was further ascertained that the beer concerned did not appear to come exclusively from one brewery, but from several. Samples of beer were obtained from a shop to which one case of illness, and that a serious one, could be clearly traced. These were sent to Professor Delépine, who succeeded in finding arsenic in considerable quantity. In the meantime I ascertained that Dr. Reynolds, to whom the whole credit of first suspecting arsenic as the cause of the illness is due, had also discovered that substance in a sample of beer from another brewery, and that he was of opinion that the illness was arsenical poisoning. The general symptoms of the cases confirm this view; the paralysis and pigmentation of the skin, running of the eyes and

nose, various skin affections, the tenderness of the muscles, and the tingling ('pins-and-needles') sensation in the hands and feet, are all known to be present in arsenical poisoning; but the two symptoms which are generally considered specially characteristic of arsenical poisoning, namely, vomiting and diarrhœa, have been entirely absent in all the cases I have personally examined but one case, where there was some diarrhœa. I was already in communication with the brewers, and I must here thank them most sincerely for the great assistance they have given me in prosecuting my inquiries, which, but for their help, could not possibly have been carried out so quickly. They threw open their breweries to me without the slightest reserve, and were most anxious that the whole matter should be cleared up and the cause discovered as quickly as possible, although they could not believe that beer could by any possibility be the cause. The sugar and sulphuric acid manufacturers have also been most willing to give me every assistance. I ascertained from the brewers that there had not been the slightest change in the method of brewing, or in the materials used, which were in every case purchased from the same firms with whom they had done business for years.

"Samples of everything used in the brewery were submitted to analysts, and it was found that arsenic was present in quantity in one sample of glucose and in one sample of inverted sugar. These two sub-

stances were obtained from the same firm of manufacturers, and I visited their works, obtaining samples of each ingredient used in the process of manufacture. It should be explained that glucose and inverted sugar, or brewers' sugar, are forms of grape sugar very largely used in brewing, though not, I am led to believe, for cheapening the production. The former is prepared by treating farinaceous substances—in this instance sago, tapioca, and maize meal—with sulphuric acid, and the latter by treating a solution of cane sugar with sulphuric acid. As the arsenic was found in both substances, and the only common ingredient was sulphuric acid, which is well known frequently to contain arsenic, suspicion fastened on this substance. This was confirmed by finding arsenic in large quantities in the sulphuric acid from the sugar manufacturer's works. Before the question can be considered finally settled, however, a great deal of work remains to be done. In the first place, it should be stated that only 2 to 6 per cent. of the affected acid is used in the manufacture of the glucose and sugar, and that only from 5 to 10 per cent. of these materials is used in the beer; so that careful quantitative analysis, for which there has not yet been time, is required to ascertain if the quantity of arsenic reaching the beer is sufficient to cause the symptoms. It should also be remembered that neither the sulphuric acid manufacturer, the sugar manufacturer, nor the brewer has altered the sources of supply of their raw materials for years, and that, so

far as I have been able to ascertain up to the present, there has been no change in any process to account for the change which must have occurred in the beer about June last.

"At the same time, to have found a poisonous substance in the beer which will account for the symptoms and to have traced that material to its source appears in all probability to have cleared the case up, especially as it has already been found that this firm of manufacturers supply direct six out of the eight breweries to which cases have been traced, and the same substance is used in breweries in Heywood and Chester, where cases have also been said to occur. An idea of the poisonous nature of arsenic is best given by stating that one grain in three gallons of beer would be a very dangerous amount. It is by no means certain yet that the firm concerned in this case is the only one whose glucose and sugar are contaminated, but as they sell their products to many brewers in this part of Lancashire the widespread incidence of the poisoning is readily explained. There appears to be no doubt that there has been no negligence, much less anything more culpable, on the part of the brewers, and it is satisfactory to have to report that every one concerned has already taken thorough precautions to prevent any further poisoning from this source. I hope to be able to report further on this matter in a short time, giving the results of the quantitative analysis and a detailed account of the cases which have come under

my notice, also the results of similar analyses of the materials used in the other breweries of the borough. In conclusion, I must thank Professor Delépine for his invaluable assistance and many suggestions; the fact that such a large number of analyses have been carried out within a week from his receiving the first sample will indicate the enthusiastic manner in which he and his staff have thrown themselves into the work. My thanks are also due to Dr. Cran, Dr. Reynolds, and other friends for their kind assistance.

(Signed) "CH. H. TATTERSALL,
Medical Officer of Health.

"*November* 25, 1900."

The *Manchester Guardian* of the 27th November 1900 published the following under the heading "Dr. Niven on the Outbreak":—

"Dr. Niven, medical officer of health for the city, stated last night that he concurred in the report of Dr. Tattersall, which he regarded as giving a full account of the disease and a satisfactory explanation of its origin. Though the samples of beer which he himself had taken from the sources of supply indicated by sufferers from peripheral neuritis had not been found by the City Analyst to contain arsenic, he was quite satisfied that a considerable quantity of beer on tap in the city was so poisoned, for he had seen the crystal in samples analysed by Professor Delépine. Instances of the disease," continued Dr. Niven, "were being reported

to him by private practitioners, who had only been able to diagnose it since the publication of Dr. Reynolds' article. Dr. Niven rather regretted the tendency to 'rush' and 'exploit' the epidemic as being inimical to deliberate scientific investigation."

And, on 3rd December 1900, the epidemic was subsiding, and the *Manchester Guardian* announced as follows:—

"The number of patients suffering from arsenical poisoning in the Manchester Royal Infirmary has now, it is stated, been reduced to ten. Two patients had so far recovered on Saturday that it was possible to remove them to the Barnes Convalescent Home, but during the day a man offered himself for treatment, whose condition was such that it was deemed necessary to detain him in the Infirmary. The number of out-patients suffering from the disease appears to be steadily decreasing. Two patients were, however, admitted on Saturday to the Workhouse Hospital at Withington, where there are a number of cases under treatment. Three new patients were also admitted to the Hope Hospital, but here, as at Withington, none of the cases are thought to be of a serious nature."

The author of this book has preferred to let the medical officers and the public press tell the tale of the epidemic; and the reader will be able to draw his own conclusions. He will no doubt have noted that Dr. Sheridan Delépine, the Professor of Pathology at

Owens College, appeared to give much satisfaction to the medical authorities after the unfortunate Public Analyst had failed to find anything to complain of in fifteen samples of beer, collected some of them on the 9th November, and the others "in the few days following." After that disappointment, there being a very great number of cases of illness in the borough, the medical officer went to consult Professor Delépine, and "samples of beer were obtained from a shop to which one case of illness, and that a serious one, could be clearly traced. These were sent to Professor Delépine, who succeeded in finding arsenic in considerable quantity." "In the meantime," Dr. Tattersall continues, "I ascertained that Dr. Reynolds, to whom the whole credit of first suspecting arsenic as the cause of the illness is due, had also discovered that substance in a sample of beer from another brewery." Very amusing is the latter portion of Dr. Tattersall's report, where he thanks Professor Delépine, and remarks, "The fact that such a large number of analyses have been carried out within a week of his receiving the first sample, will indicate the enthusiastic manner in which he and his staff have thrown themselves into the work."

In fact, for the purpose of dealing with the epidemic, the Public Analysts of Manchester and Salford seem to have been pushed aside and Professor Delépine and his staff employed in their places.

Under these circumstances some interest is attached

to a paper published by Professor Delépine, on 12th January 1901, in the *British Medical Journal*, in which there is a description of Reinsch's test used "to estimate approximately the quantity of the poison." From this paper may be quoted:—

"Reinsch's Process.—The selection of a proper method for the detection of arsenic in beer was not less important. The two most reliable qualitative methods are undoubtedly the Marsh's and the Reinsch's, but neither of these had been extensively used for the purpose of estimating the amount of arsenic in beer and some of the organic substances we had to deal with. At any rate, references to such experiments were not easy to find.

"Several comparative trials showed me that the Reinsch's test was eminently applicable to the detection of arsenic in beer, glucose, hops, and all the other organic and inorganic compounds I had to deal with. With regard to Marsh's test *it was inapplicable to beer which had not been previously treated so as to break up the organic matter.* I therefore thought that if the first method could be made to reveal sufficiently small quantities of arsenic in beer, and be used to estimate *approximately* the quantity of the poison in a moderate amount of fluid, it would be preferable to the latter, which, though very delicate, was more complicated, and would probably introduce greater sources of experimental error. By conducting the Reinsch's test with care, I found that it was easy to detect the

presence of arsenic in 100 c. cm., and even as little as 20 c. cm., of some of the suspected beers. On the other hand, no distinct trace of arsenic could be found in as much as 200 c. cm. of beer brewed in Bavaria, where the use of malt substitutes is prohibited by law."

The passage *italicised* was not *italicised* in Dr. Delépine's text. It is a curiosity. Marsh, when he was alive, claimed for his process that it was applicable to liquids wherein the organic matter was intact; and, as the reader may observe on turning back to Marsh's paper, which is republished *in extenso*, Marsh asserted that he had successfully operated upon "three pints of very thick soup."

The statement of Dr. Delépine's, that Marsh's test is inapplicable to beer which had not been previously treated so as to break up the organic matter, shows that his knowledge of the test was not derived from Marsh's original paper, but must have come second-hand from some inaccurate text-book.

Having in that manner disposed of Marsh's test, Professor Delépine describes his own method of working the Reinsch test, quantitatively, as he apparently imagines. *He* makes a standard solution of arsenious acid in pure beer, containing one part of As_2O_3 in one million parts of beer. Then he places his strip of copper in 100 c. c. of the standard solution, and in that way extracts the arsenic from the solution and attaches it to the copper. Next he heats the copper in a peculiar

copper vessel and causes the As_2O_3 to sublime and form a film on a glass plate which is finally viewed under the microscope.

The film on this glass plate is to be compared with the films caused by the different samples of beer which he desires to investigate. His own words will best explain the mode of operation: "To estimate rapidly quantities of As_2O_3 above one part per one million it is only necessary to reduce the quantity of beer used until one finds the smallest amount that will give a deposit on copper yielding a sublimate of As_2O_3 corresponding to the standard deposit obtained from 100 c. c. of the $\frac{1}{1000000}$ solution. If 25 c. c. of beer are sufficient to give such a result, it may be assumed that there are at least four parts of arsenious acid in one million parts of beer."

It is further explained that the 25 c. c. of suspected beer might, of course, have been diluted with water and so expanded to give a volume of 100 c. c. before putting the slip of copper-foil into it; but he thought, and found, that it was better not to dilute in that way.

Dr. Delépine would seem to be so well satisfied with the results of his work that he did not confine his operations to suspected beer and suspected glucose, but actually took in hand the suspected sulphuric acid reported to be the original fountain of the poisonous outbreak in Manchester and Liverpool. Further on may be read: "By the modification of Reinsch's method

just described we found that the amount of arsenious acid in one sample of H_2SO_4 was about 2 per cent." And there is a pretty little picture of the photograph labelled "Fig. 4. Margin of one of the six films obtained from $\frac{1}{20}$ of the copper used in testing 2 c. cm. of the sulphuric acid used in the preparation of the above glucose."

The objections are very serious and far-reaching.

If the slip of copper were capable of extracting all the arsenic from the beer, and then, on being heated in the little copper receptacle, passed on all the arsenic to the microscope-slides, and if all the arsenic on the slide assumed the crystalline state yielding crystals of equal size, then the method would have claims to be regarded as fairly quantitative. Failure in complying with any of these conditions is fatal to the quantitative character of the method; and there is failure in two of the conditions. The copper slip does not exhaust the beer and remove all the arsenic. Neither does it always remove the same fraction of the total arsenic in the beer, which might be a practicable substitute for total extraction.

There is also the greatest uncertainty as to how much or how little of the arsenic reaching the microscope-slides will take on the crystalline form. Very slight changes in the physical conditions have much effect upon the production of crystals; whether the crystals shall be large or small depends upon many other circumstances than the mere quantity of arsenious

acid which happens to be present in the liquid under investigation.

When the microscope is called in to supplement and complete a process of chemical analysis it brings with it its own peculiar difficulties and limitations. The prettiness of the picture of the slide with microscopic objects upon it is calculated to absorb too much attention, and sometimes so disturbs the judgment that the sense of proportion with the appreciation of numbers suffers from a sort of temporary paralysis.

The author does not suggest that Dr. Delépine suffers from this disturbance, and indeed assumes that he does not suffer in that way.

In the paper there is a little picture of the photograph from the slide showing "Sublimate obtained from half of the copper used in testing 50 c. cm. beer containing one part of As_2O_3 in one million parts of beer."

The paper does not give all the numerical data required for a calculation of the weight of the yield of arsenical crystals in the film arising from the heated copper, but the requisite data are most probably in the possession of Dr. Delépine, who no doubt could make the calculation if he were disposed to take the trouble to do so.

The result of such calculations would show that only a trifling percentage of the As_2O_3 put into the standard arsenical beer is ultimately to be found in the film on the glass plate in the form of crystals

of As_2O_3, the greater portion of the arsenic being either not deposited at all, or else deposited in the amorphous state.

Reference to Chapter I., pages 16 and 17 (where the peculiarities of the allotropic states of As_2O_3 are mentioned), will suggest to the reader how very seriously any attempt to gauge the quantity of As_2O_3 by the apparent magnitude of the crystals must be interfered with. What possible value can be attached to the quantity of the crystals of As_2O_3 if the operator is in doubt whether 5 per cent. or 95 per cent. of the As_2O_3 on the plate will assume the crystalline form? The numerical results of these attempts at quantitative valuation by these so-called improvements of Reinsch's test are mere nonsense figures.

In Chapter II., page 58 and following pages, this question is further dealt with. And the reader will understand that, in the opinion of the author of this book, the chemical investigations into the circumstances attending this epidemic have been of the most unsatisfactory character, and utterly unworthy of the country of which James Marsh was a native. The actual facts brought out by the investigation into the nature and cause of the epidemic are, as yet, very limited.

One fact has come out with great distinctness, viz. that not always has the sulphuric acid employed in the preliminary transformation of starch and cane sugar been the acid which is approximately free from

arsenic. Whether, however, the acid has ever contained anything like 2 per cent. of arsenious acid, or of arsenic in other forms, is, no doubt, within the knowledge of some persons in the North of England; but no satisfactory evidence has, so far as the present writer knows, come before the public.

Incidentally, as a kind of by-result of the epidemic, the important observation of Dr. Reynolds deserves notice. That much of that which has heretofore been set down as chronic alcoholism is in reality chronic poisoning with arsenic has been proved almost to demonstration by Dr. Reynolds.

Bearing in mind the general diffusion of arsenic, it must be obvious that we all take minute doses of arsenic with our daily food; and if the power of disposing of arsenic were taken away from us, we should in course of time begin to suffer from arsenical poisoning. In that manner it may be explained how indirectly an excessive drinker might suffer from arsenical poisoning, notwithstanding that his drink might be "practically non-arsenical." The whole question of poisoning with arsenic is a wide and difficult subject. Can the arsenic be stored up in our bones? Can it to any extent replace the phosphorus in the phosphate of lime? Do the Styrian arsenic-eaters acquire arsenical bones, or do they continually throw off the arsenic in some non-poisonous shape?—these are questions which have to be answered. The assimilation of mineral matter has at different

times attracted the attention of chemists, and in this connection the author calls to mind a paper read to the Physiologial Section of the British Association in the year 1875 by his colleague, W. J. Cooper, wherein questions of this kind were discussed.

THE END.

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